



Japanese Technology Evaluation Center

NASA**JTEC**

JTEC Panel Report on

Advanced Composites In Japan

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JAPANESE TECHNOLOGY EVALUATION CENTER

- SPONSOR** The Japanese Technology Evaluation Center (JTEC) is operated for the Federal Government by Loyola College to provide assessments of Japanese research and development (R&D) in selected technologies. The National Science Foundation (NSF) is the lead support agency. Other sponsors include the Defense Advanced Research Projects Agency (DARPA), the National Aeronautics and Space Administration (NASA), the Department of Commerce (DOC), the Department of Energy (DOE), and the Office of Naval Research (ONR).
- PURPOSE** JTEC assessments contribute to more balanced technology transfer between Japan and the United States. The Japanese excel at acquisition and perfection of foreign technologies, but the U.S. has relatively little experience with this process. As the Japanese become leaders in research in targeted technologies, it is essential that the United States have access to the results. JTEC provides the essential first step in this process by alerting U.S. researchers to Japanese accomplishments. JTEC findings can also be helpful in formulating governmental research and trade policies.
- APPROACH** The assessments are performed by panels of about six U.S. technical experts in each area. Panel members are leading authorities in the field, technically active, and knowledgeable about Japanese and U.S. research programs. Each panelist spends about one month of effort reviewing literature, making assessments, and writing reports on a part-time basis over a twelve-month period. All recent panels have conducted extensive tours of Japanese laboratories. To provide a balanced perspective, panelists are selected from industry, academia, and government.
- ASSESSMENTS** The focus of the assessments is on the status and long-term direction of Japanese R&D efforts relative to those in the United States. Other important aspects include the evolution of the technology, key Japanese researchers and R&D organizations, and funding sources.
- REPORTS** The panel findings are presented to workshops where invited participants critique the preliminary results. Final reports are distributed by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 (703-487-4650). The panelists also present technical findings in papers and books. All results are unclassified and public.
- STAFF** The Loyola College JTEC staff members help select topics to be assessed, recruit experts as panelists, organize and coordinate panel activities, provide literature support, organize tours of Japanese labs, assist in the preparation of workshop presentations and in the preparation of reports, and provide general administrative support. Dr. Alan Engel and Ms. Kaori Niida of International Science and Technology Associates provided literature support and advance work for this panel.

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FINAL REPORT

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FOREWORD

This is the latest in a series of Japanese technology assessments that we have been conducting under the JTEC program since 1984. In 1983 George Gamota convinced Frank Huband of the National Science Foundation (NSF) and Bill Finan, his counterpart at the Department of Commerce, that the Nation must do more to monitor Japanese research. The methodology chosen was to use an expert panel to take a snapshot of the status of Japanese research in a critical technology by an intensive study--and to communicate the implications of the Japanese efforts to policy makers in government and industry. To provide the logistics support we contracted with the Science Applications International Corporation (SAIC).

We will review the JTEC studies that are available, but will not attempt to summarize each of their findings in a sentence or two--the full reports are available from NTIS. We will make a few overall comments on our findings at the end.

Our first effort was a series of four panels in 1984 and 1985. We asked David Brandin, then at SRI International, to chair a panel which would take a look at the broad range of computer science. Dale Oxender at Michigan chaired a panel on biotechnology. Jim Nevin at the Draper Lab led a group that looked at mechatronics, which the Japanese define as the union of electrical and mechanical engineering--things like robotics and flexible manufacturing systems. Finally we had a group, jointly chaired by Bill Spicer of Stanford and Harry Weider of UCSD, research Japanese progress on non-silicon microelectronics, such as gallium arsenide devices and optical electronics devices.

In 1986 the National Science Foundation took over the role as lead agency, and with additional funding from DARPA, we organized six panels during the next three years. Our telecommunications panel was chaired by George Turin, then Dean of Engineering at UCLA. The group on advanced materials (primarily polymers) was chaired by Jim Economy of IBM. Under Marvin Denicoff of Thinking Machines, Inc., our second computer panel took a focused look at parallel architectures, particularly the Fifth Generation Project. This group was the first to include a tour of Japanese laboratories as a formal part of its procedures, which proved to be so illuminating that all subsequent panels have taken a similar trip there. In 1988 George Gamota and Wendy Frieman compiled the results of the first six panels, with some cross-cutting observations, into the book, *Gaining Ground: Japan's Strides in Science and Technology*, published by Ballinger.

The Japanese ERATO research initiative consists of more than twenty projects intended to foster creativity and cooperation in more basic research, particularly in electronic materials and biotechnology. We appointed joint chairmen, Bill Brinkman of Bell Labs and Dale Oxender of Michigan, to cover these areas. Computer-aided design and computer-integrated manufacture of semiconductors in Japan was studied by a panel under Bill Holton of the Semiconductor Research Cooperative. Finally research in advanced sensors was assessed by a panel under Laurie Miller of Bell Laboratories.

By 1989 the project had proven to be successful enough to warrant establishment of the Japanese Technology Evaluation Center at Loyola College under a grant from NSF with additional funding from DARPA, NASA, the Department of Commerce, and the Department of Energy. The current phase includes ten panels. High definition products and systems have been assessed by a group under Dick Elkus. Millie Dresselhaus of MIT has compiled a report on superconductivity applications. A group chaired by Charles Merkle of Penn State has recently completed an assessment of space and transatmospheric propulsion technology in Japan. Our third computer panel supported the implementation of the science and technology treaty signed by President Reagan and Prime Minister Takeshita in Toronto in 1988 by identifying opportunities for joint research in advanced scientific computing. It was chaired by Mike Harrison of Berkeley. A report on nuclear power generation in Japan was authored by a panel under Kent Hansen at MIT. The present report on advanced high temperature composite materials has been prepared by a group under Judd Diefendorf at Clemson University. A Panel chaired by Red Whittaker of Carnegie Mellon University has just completed its report on space robotics, and Richard Tucker of the University of Texas is leading a panel on construction technologies. We have recently initiated panels on machine translation research, bioprocess engineering, and database technology.

Finally, we now have underway a study of nuclear power instrumentation and control technology in Europe and Canada, our first experiment at applying the JTEC methodology to countries other than Japan. With support from the Department of Energy, the final product from this new study will be integrated with the results of the present report on nuclear power in Japan to produce a global comparative assessment of the status of research in nuclear power instrumentation and controls.

Throughout this phase of JTEC, literature support and advance work in Japan are being carried out by Dr. Alan Engel and Ms. Kaori Niida of ISTA, Inc., by Dr. Robert Lewis and Ms. Keiko Koike of the Tsukuba Research Consortium, and by Mr. Cecil Uyehara of Uyehara International Associates. Advance work for the Soviet Union is being supplied by the USSR Nuclear Society in Moscow, and

American Trade Initiatives of Alexandria, VA is providing these services for the rest of Europe.

We have seen Japanese research make great progress over the course of the JTEC studies. In 1984 the conventional wisdom held that the Japanese excelled at acquiring foreign technologies, performing competent applied research to perfect them, and then developing manufacturing techniques to make high-quality products. Our early panels frequently confirmed that model, but began to report centers of excellence in more basic research as well, particularly in areas targeted by the Japanese for long term commitments. Now we are seeing more technologies where the Japanese are using the revenue stream from their favorable balance of trade to strengthen their basic and applied research capabilities. As these investments produce innovations, we in the United States must learn how to better transfer Japanese and other foreign technologies to the U.S. JTEC can be a useful first step in that process, by identifying areas where the Japanese have the world's best technologies.

Of course, many other countries besides Japan have traditions of excellence in science and technology. Though Japan remains the focus of the JTEC program, we feel that the JTEC methodology may be equally relevant as applied to other countries. In general, the United States can benefit from a better understanding of cutting edge research that is underway outside its borders. Improved awareness within the United States of international developments in science and technology can in turn significantly enhance the scope and effectiveness of international collaboration in research and development, and thus benefit all of our international partners in collaborative R&D efforts.

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EXECUTIVE SUMMARY

ADVANCED COMPOSITES RESEARCH AND DEVELOPMENT IN JAPAN

The JTEC Panel on Advanced Composites visited Japan and surveyed the status and future directions of Japanese high performance ceramic and carbon fibers and their composites in metal, intermetallic, ceramic, and carbon matrices. The Panel's interests included not only what composite systems were chosen, but also how these systems were developed, and who made the selection and investment decisions. The quality, enthusiasm and number of people, as well as their funding and results, were noted in basic research, advanced development, products, and manufacturing.

Much of the motivation of the Japanese stems from the fact that Japan has insufficient land to feed its people, and has few natural resources. Japan must survive by importing food and materials, and by exporting manufactured products. However, Japan is faced with the loss or at least erosion of its consumer electronics exports to Pacific Rim countries. Either new, more sophisticated products must be developed, or a major new market is required to maintain or increase the Japanese standard of living. One such market is in aerospace.

The Japanese have an ambitious space program. More importantly, they have also initiated development of a hypersonic civilian aircraft to be completed by 2005. A major factor in these programs is new materials, one of three areas selected by MITI for a major national development investment. The Japanese believe that technological superiority in space structures and launch systems, and particularly in hypersonic vehicles, will allow them to become a dominant force in the aerospace market.

Both Japanese industry and government have a long term philosophy to build for the future at the expense of short term gains. The MITI new materials thrust is scheduled to extend for ten years, a longer time than would be possible in the U.S. The Japanese encourage and support parallel approaches to materials research and technology which often involve overlapping activities between several groups with a sharing of information at the "pre-competitive" stage. By contrast, the U.S. often tries to select one "best" approach initially and then frequently finds that other options are needed.

For Japanese government programs, requirements are usually set at a modest, realistic, and attainable level. In this way, government and public support is maintained. Initial goals for the new high temperature materials program have been set very high by MITI, however. The consensus is that these goals will be revised downward to what can be achieved. Unlike the U.S., the goals are not driven by the requirements of a specific system.

Direct Japanese government funding is quite small for new materials, at least in comparison to the U.S. However, Japanese government funding figures usually do not include personnel costs, which are covered as part of a base budget. Thus, Japanese funding for new materials research is actually quite substantial in terms of resources expended. In addition, government funding focuses on areas of national interest, and a strong national unity drives industry to make much larger contributions to the support of new materials research and technology. Thus, the government funds have high leverage.

The Japanese make the most of what they have. Even if a material is not optimum, they will try to find an application, so that they get the manufacturing experience to produce a lower cost, more reliable product. Hence, there is often less emphasis on basic science, and more on manufacturing and large scale pilot plants. Although there is a wide diversity, there tends to be more learning by doing, and fewer analytical studies.

Some previous MITI materials programs have led to new consumer markets and thus to substantial returns on the government investment. The Japanese have learned skills, especially in manufacturing, and have formed technical teams within and across industries which remained intact for the long periods of time required for market development and exploitation. The new high temperature materials program is quite different in that, while these materials may be an enabling technology for a hypersonic transport vehicle, they may only be produced in small quantities. Japanese companies that would only be materials producers may have to re-examine the question of national commitment versus profit. For the large U.S. aerospace companies, acquisition of these new materials from reliable sources will be a problem due to the potentially slow payback on investments in needed manufacturing equipment. By contrast, the large, well-funded, and vertically integrated Japanese companies can set up to produce the materials and aircraft structures internally.

A strong carbon and fiber industry makes Japan the leader in carbon fiber technology. Japan has initiated an oxidation resistant carbon/carbon composite program. Their outstanding technical base in carbon technology should allow them to match present technology in the U.S., and to introduce lower cost

manufacturing methods during this program. However, this JTEC Panel did not see any research on innovative approaches to oxidation protection.

Japan manufactures more polymeric precursor ceramic fibers than other countries. For high-temperature aerospace applications, these fibers have serious property and compatibility limitations. However, the Japanese government does not intend to fund fiber development, and the development of these fibers by industry is on the wane. The Japanese will stay with the available fibers for composites. Ceramic and especially intermetallic matrix composites are not receiving much attention yet, but may soon. Monolithic ceramic research and development activity remains at a high level. High temperature monolithic intermetallic research is just starting, but with some notable products in titanium aluminides.

Matrixless ceramic composites was one novel approach that the JTEC Panel noted. Technologies for high temperature composites fabrication exist, but extensive numbers of panels or parts had not yet been produced at the time of the Panel's visit. Lack of a commercial market, not the availability of technology, has decreased the interest of Japanese companies in aluminum matrix composites that have lower temperature capabilities.

In summary, Japanese government and industry have selected aerospace as an important future industry. Materials are an enabling technology for a strong aerospace industry. Japan has initiated a program to develop high temperature composites. This long-term program is staffed by hard-working, well-trained scientists and engineers in well-equipped laboratories. The goals for the program are ambitious, and the program is just starting, but its progress should be closely monitored in the United States.

SPECIFIC R&D COMPARISONS

The following includes a discussion of the principal findings of each chapter of the full report of the JTEC Panel on Advanced Composites. Chapter 1, by R. Judd Diefendorf and R. Byron Pipes, includes an introduction to the scope of the Panel, a discussion of funding for advanced composites R&D in Japan, and an overview of advanced composites manufacturing in Japan.

Reinforcements

High temperature/high performance composites for aerospace applications are critically dependent on the availability of strong, lightweight fibers. Since Japan is embarking on several advanced aerospace efforts, e.g., Mach 4-6 hypersonic

technology development, there was a desire to survey their past fiber accomplishments and examine any available information on efforts presently underway.

Chapter 2, by Salvatore J. Grisaffe, first summarizes the issues and concerns surrounding high temperature fiber availability. Then examples of available data on Japanese fibers are presented. Where comparisons are possible, these fibers are compared to those manufactured in the U.S. In general, Japan has done well in developing a number of useful fibers--primarily via the polymer precursor approach. However, neither the Japanese nor the U.S. fibers are adequate to meet rigorous projected high temperature, long term aerospace service. The Japanese, however, appear to be learning how to produce good quality fibers in reasonable quantities. They also appear to be learning how to fabricate lower temperature composites with these fibers. And, they are starting efforts to develop insights into advanced composite fabrication and higher temperature composite durability (the latter through parallel studies of functionally gradient materials). Such insights will help them exploit improved fibers as they become available.

Ceramic Matrix Composites

In Chapter 3 William B. Hillig notes that Japanese interest in ceramic composites is part of their larger interest in high temperature, high performance structural materials for power generation, transportation, and aerospace applications. U.S. researchers tend to strive for major "breakthroughs," while the consensus in Japan is that enhancing the toughness of the best already available monolithic structural ceramics is the best approach. Even though Japan is a prime supplier of the continuous high performance, high temperature fibers that fuel much of the ceramic composites effort in the United States, the Japanese effort has instead focused on the use of SiC and Si₃N₄ whiskers and particulates. This strategy is consistent with the philosophy of working with and perfecting materials that are available and economically viable, rather than striving for the ultimate, but high-cost, material for which the total demand would be so narrow that its production might require subsidy.

Significant effort is also being devoted to the processing of hybrid ceramic/metal composite systems. Sophisticated techniques are being developed for making functionally gradient materials (FGM) that gradually transition from ceramic to metal properties. These FGMs are designed to overcome the severe thermal expansion mismatch problems in joining metal to ceramic parts in the envisioned high temperature heat engines. A separate pioneering processing effort is directed at making the rather intractable high temperature, high performance composite materials into useful shapes that will be needed for the above engines. This effort

involves combining self-propagating high temperature synthesis (SHS), with hot isostatic pressing (HIP) to produce high quality material in the desired complex shapes.

Metal and Intermetallic Matrix Composites

Chapter 4, by John H. Perepezko, covers metal and intermetallic matrix composites. Japan's entry into metal matrix composites occurred about a decade later than that of the U.S. However, the Japanese have more than made up for lost time in all aspects of composites. An empirical approach is generally favored over one guided by theoretical modeling. While Japanese efforts are directed toward long-term benefits, they are also focused on specific commercial applications. In general, widespread commercial application of metal matrix composites has not developed in Japan. The current focus of activity is directed towards the development of lower cost production methods. The Japanese R&D programs also emphasize self-sufficiency in components. The MITI-orchestrated national projects have been effective. The new initiative on high temperature materials has strong support. Some early successes have been achieved with intermetallic alloys that yield enhanced performance in high temperature turbine applications. A large scale research effort is underway on functionally gradient materials. This approach may offer a cost-effective method of producing high temperature materials with tailored properties.

Carbon-Carbon Composites

Chapter 5, by James E. Sheehan, notes that carbon fiber-carbon matrix (C-C) composites are strong, light-weight, very high temperature materials that are important for a variety of military and aerospace applications. Commercial aerospace uses are expected to broaden in the future, and if C-C production costs can be reduced it is likely that significant non-aerospace applications will be developed. The Japanese consider C-C composites to be enabling for their growing aerospace activities, and many also view these materials as potentially important in several manufacturing industries and as components in special products and systems.

The Japanese have been fabricating, characterizing, and testing C-C composites for almost two decades. Most of the work reported by Japanese investigators that has appeared in English is of a basic nature and little has been discussed concerning processing technology or the production of articles or components. However, the visit of the JTEC panel to Japan and recent descriptions of Japanese aerospace activities show that the Japanese are fabricating C-C articles by methods similar to those practiced in the United States.

The fabrication of C-C composites has been a major government funded activity in the United States for almost 20 years, and a mature domestic industry exists to manufacture large, complex C-C shapes. In contrast, the Japanese emphasis on C-C components manufacturing is only recent and is due to combined government and private support of projects that are considered essential to establishing a competitive position in aerospace. Although several Japanese companies possess the facilities and basic understanding to produce C-C components, a historical lack of applications and design experience create a current disadvantage for Japan.

The factors that drive C-C manufacturing innovation in Japan include a fundamental concern with production costs and associated efforts to identify commercial non-aerospace applications for C-C composites. The development of new cost-effective fabrication methods that could open the door to C-C uses in commercial industries is a trend in Japan that appears to be absent in the United States. Clearly, even if new and significant industrial uses are not realized, the Japanese aerospace industry is likely to benefit from improvements in C-C manufacturing methods.

CHAPTER 1

INTRODUCTION TO JAPAN'S ADVANCED COMPOSITES PROGRAM

R. Judd Diefendorf and R. Byron Pipes

SCOPE OF THE STUDY

The initial meeting of the JTEC Panel on Advanced Composites was held on September 8, 1989, at the National Science Foundation in Washington, DC. Duane Shelton of JTEC defined the goals of JTEC; Dan Mulville from NASA, the major sponsoring agency, presented NASA's interests in composite materials; and Ben Wilcox from DARPA summarized the interim conclusions of two U.S. Government teams interested in composites that had recently visited Japan.

Due to budget constraints, it was decided that the scope of the JTEC panel's investigations would be limited to high-temperature advanced composites. The primary goals of this panel were to study past and current Japanese programs in high-temperature advanced composites, to compare their present technological status with those of the United States, and to predict the consequences of these programs on the future technological capability of Japan. Secondary goals were to investigate the criteria for program selection, funding levels and cycles, organization, and evaluation. The information in this report hopefully will increase the awareness of the U.S. technical and policy communities regarding Japanese efforts in high-temperature advanced composites, and the potential consequences for the U.S. space, air, ground, and sea transportation industries, as well as for other important industries such as power generation.

Each of the JTEC panel members was assigned responsibility for a major topic area, and these topic areas serve as the titles for the chapters in this report. In addition, each panel member was assigned to serve as a reader and critic for the report on another of the major topic areas. The assignments are shown in Figure 1.1.

The panel's trip to Japan was scheduled for February 3-10, 1990. Based on information gathered at the Society for Advancement of Material and Process Engineering (SAMPE) meeting the previous December and the panel members' previous knowledge of Japanese research on advanced composites, an extensive list of Japanese laboratories performing R&D on advanced composites was prepared (Fig. 1.2; locations are shown in Fig. 1.3).

The large number of Japanese ministries and laboratories on this list required that the panel be separated into three groups of two members each, although the personnel makeup of each group varied during the trip. Even so, and with as many as three visits per day, visits to a number of laboratories had to be omitted, especially if they required lengthy travel or if the specialties of the laboratories were similar to those of other laboratories more easily visited.

The panel visits and detailed itineraries for each panel member were arranged by Ms. Kaori Niida of International Science and Technology Associates (ISTA). The visits included two universities, nine industrial and seven government laboratories, and presentations by the Agency for Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI). See Appendix B for the list of Japanese sites visited by the panel.

While these visits allowed the panel access to a wide variety of Japanese R&D in high-temperature composites, the panel often had little time for in-depth discussions. Furthermore, none of the panel members spoke Japanese, which might have allowed the panel members to engage in more philosophical probing. Nevertheless, certain common observations and conclusions were independently made by the panel members, even though they visited different facilities and were separated from each other much of the time. These conclusions are summarized in the Executive Summary.

A wrap-up session was held by the panel members in Japan on the sixth day of the trip. After returning to the United States, panel members exchanged their notes from the Japan trip. On March 26, 1990, the panel held a final meeting to discuss conclusions and to coordinate the oral presentations. Panel members gave their oral presentations at a final workshop on March 27, 1990, in Washington DC, at the National Science Foundation.

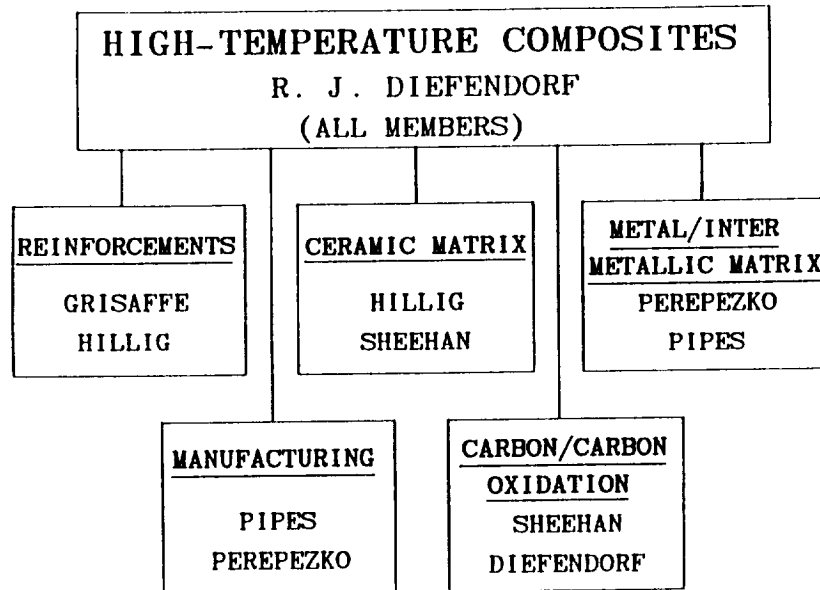


Figure 1.1. Primary and Secondary Topic Assignments for JTEC Panelists

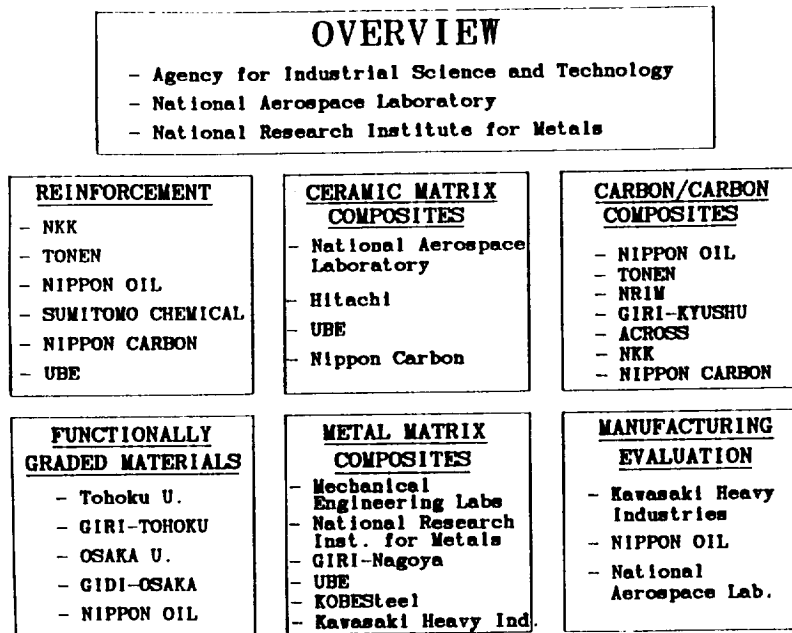


Figure 1.2. Japanese Agencies and Firms Engaged in Advanced Composites R&D

CENTERS OF COMPLEX COMPOSITES ACTIVITY IN JAPAN

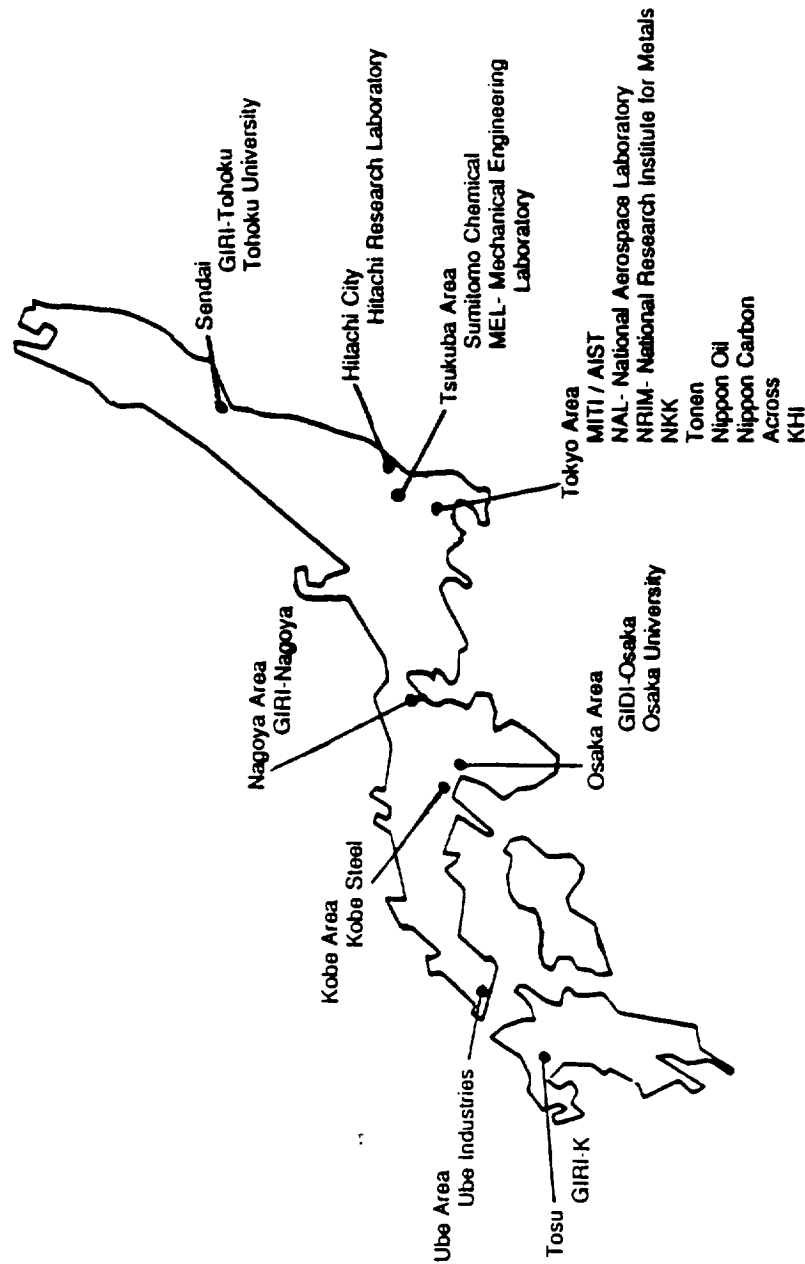


Figure 1.3. Locations of Japanese Laboratories Engaged in Advanced Composites R&D

JAPAN'S ADVANCED COMPOSITES FUNDING

In Japan, as in the United States, research and development on high-temperature composites is funded by both government and industry. There are some notable differences, however. While government agencies in both Japan and the United States set broad national goals, the national goals selected in Japan tend to be related to the general economic welfare of the country 10-15 years in the future. The national goals in the United States for high-temperature composites R&D are based largely on defense requirements for the next five-year period. Japanese choices are made to win an economic competition, while U.S. decisions are based on supporting potential military conflicts.

The Japanese government agencies often fund at what appear to be relatively low levels in broad programs to develop the selected areas. Because of the potential for new, commercially valuable technology and a strong commitment to the welfare of the nation, Japanese industries augment the government programs with their own funds. One Japanese company stated that it spent two to four times the money it received from government grants for composites R&D. By contrast, the U.S. government must often pay the major portion of an R&D program for defense, because no large consumer market may exist for the technology being developed, and industries will not invest their own resources. Hence, the funding levels of the Japanese government programs may appear to be quite small when compared to those in the United States, but for the reason cited and others, the effort expended on the programs is much higher in Japan than what might be inferred.

The overall Japanese government budget for research and development increased over the period 1980-1988 at a rate of 5-6 percent per year. However, when normalized by the annual gross national product, the increase was more modest, varying from about 0.48 percent in 1980 to 0.57 percent in 1988 (Fig. 1.4). By contrast, Japanese industrial R&D expenditures are a much larger percentage of the GNP and have increased at a faster rate. The total percentage of GNP for research and development funding by government and industry in Japan was about 2.8 percent in 1988, slightly higher than the combined total in the United States. However, in the United States the relative contributions of government and industry are about equal. Although the Japanese industrial R&D expenditures would appear to be relatively higher than Japanese government funding, private expenditures are not included in this JTEC analysis.

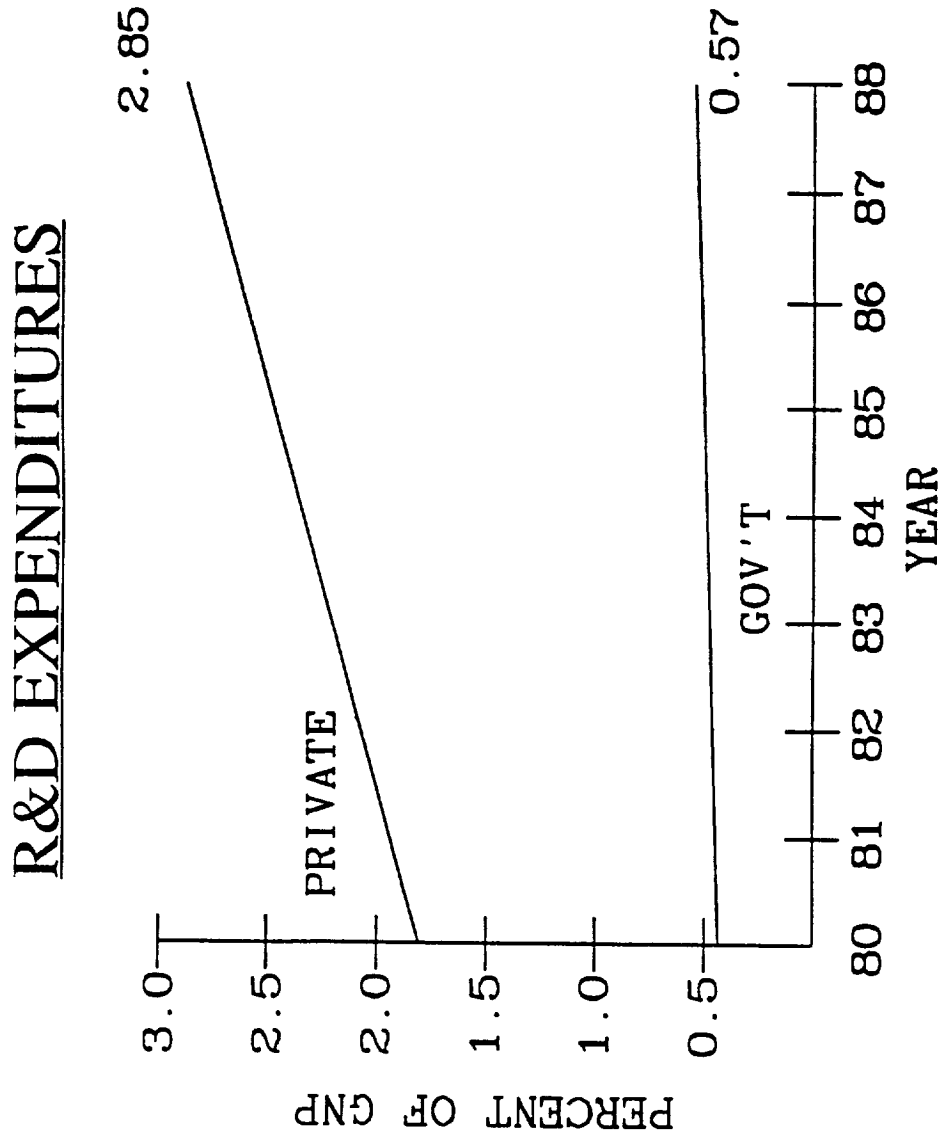


Figure 1.4. Overall R&D Expenditures in Japan (Source: Refs. 1.1 & 1.2)

There are three Japanese government agencies which have impact on the funding for high-temperature advanced structural composites: the Ministry of Education, Science, and Culture; the Science and Technology Agency (STA); and the Ministry of International Trade and Industry (MITI). Overall science and technology expenditures for these agencies are shown in Table 1.1.

Table 1.1
FY1989 Japanese Science and Technology Funding
(in millions of yen)

Agency/Ministry	Total Funding	% Increase over FY 1988
Ministry of Education	854,322	5.1
Science & Technology Agency	466,623	6.0
Ministry of International Trade and Industry	233,640	5.6

Source: Ref. 1.3

While some government programs are easily identified as being related to high-temperature advanced structural composites, especially the special programs within MITI, the expenditures for the advanced composites area in the Ministry of Education and the Science and Technology Agency could not be identified. The total expenditure by MITI specifically in the advanced composites area was ¥301 million in 1989, and at least a fraction of its ¥1,149 million High-Performance Ceramics program had technology pertinent to advanced composites.

The Japanese government has instituted a number of programs grouped together under the title, "Promotion of Technological Development in the Private Sector." They are based on tax incentives and low-cost financing. Since 1967, the tax system has allowed for a special tax deduction for experimental research. There has been a deduction for R&D facilitation costs in fundamental technologies since 1985. The low-cost financing is possible through four programs:

- 1951--Financing of Enterprises for New Technology
- 1968--Domestic Production Technology Promotion
- 1983--Financing for Promoting Industrial Technological Development
- 1985--Financing for the Japan Key Technology Center

In addition, the Japan Key Technology Center is a source of capital investment and conditional interest-free loans for programs which have successfully passed the R&D stage. For example, STA and the Key Technology Center provide 70 percent

of the funding for production capability for 3-D weaving for the spaceplane, thus drastically reducing private company risks.

GOVERNMENT GOALS AND PROGRAMS

The Japanese government plays a primary role in setting goals and priorities for the future welfare of Japan. In a complex system of agencies (Fig. 1.5) whose functions often overlap, strong but constructive competition exists. However, from the common goal of providing the Japanese people with a high standard of living in the future emerges a national policy with long-range goals and planning.

The Ministry of Education, Science, and Culture provides support to the national universities through an annual base budget for research, as well as through competitive grants-in-aid which channel funds into selected areas. All the national universities perform R&D in high-temperature composites technology. Also, the Institute for Space and Astronautical Sciences (ISAS) is an inter-university research institute under the Ministry of Education. While its purpose is not to develop high-temperature advanced structural composites, it performs research, development, and launching of rockets and satellites. These responsibilities do provide input for future materials requirements for launch and space systems.

The Science and Technology Agency has overall responsibility for aeronautics and astronautics. Both the National Aerospace Laboratory (NAL) and the National Space Development Agency of Japan (NASDA) are associated with it. NAL is the lead laboratory for aero/astronautics in Japan. NAL evaluates the mechanical and environmental behavior of new composite materials developed by industry that might be used in aerospace; it therefore has a strong influence on materials selection. NASDA develops satellites and their launch vehicles, conducts the launches, and controls the tracking of the satellites. While NASDA is a "systems" agency that uses proven and practical off-the-shelf materials, Japanese rocket engine turbomachinery has incorporated advanced materials. Moreover, the Japanese have realized that high-performance composite materials are often the enabling technology for launch vehicle engines (Ref. 1.4).

The Ministry of International Trade and Industry has responsibilities for development of creative new technologies "to maintain and strengthen the foundation for further economic and social development" (Ref. 1.3). MITI has nineteen major projects, three of which directly involve high-temperature advanced composites or technology associated with it. The three projects are administered by the Agency of Industrial Science and Technology (AIST). In addition, sixteen government laboratories are funded through AIST. Six of these laboratories are performing composites-related R&D (Table 1.2).

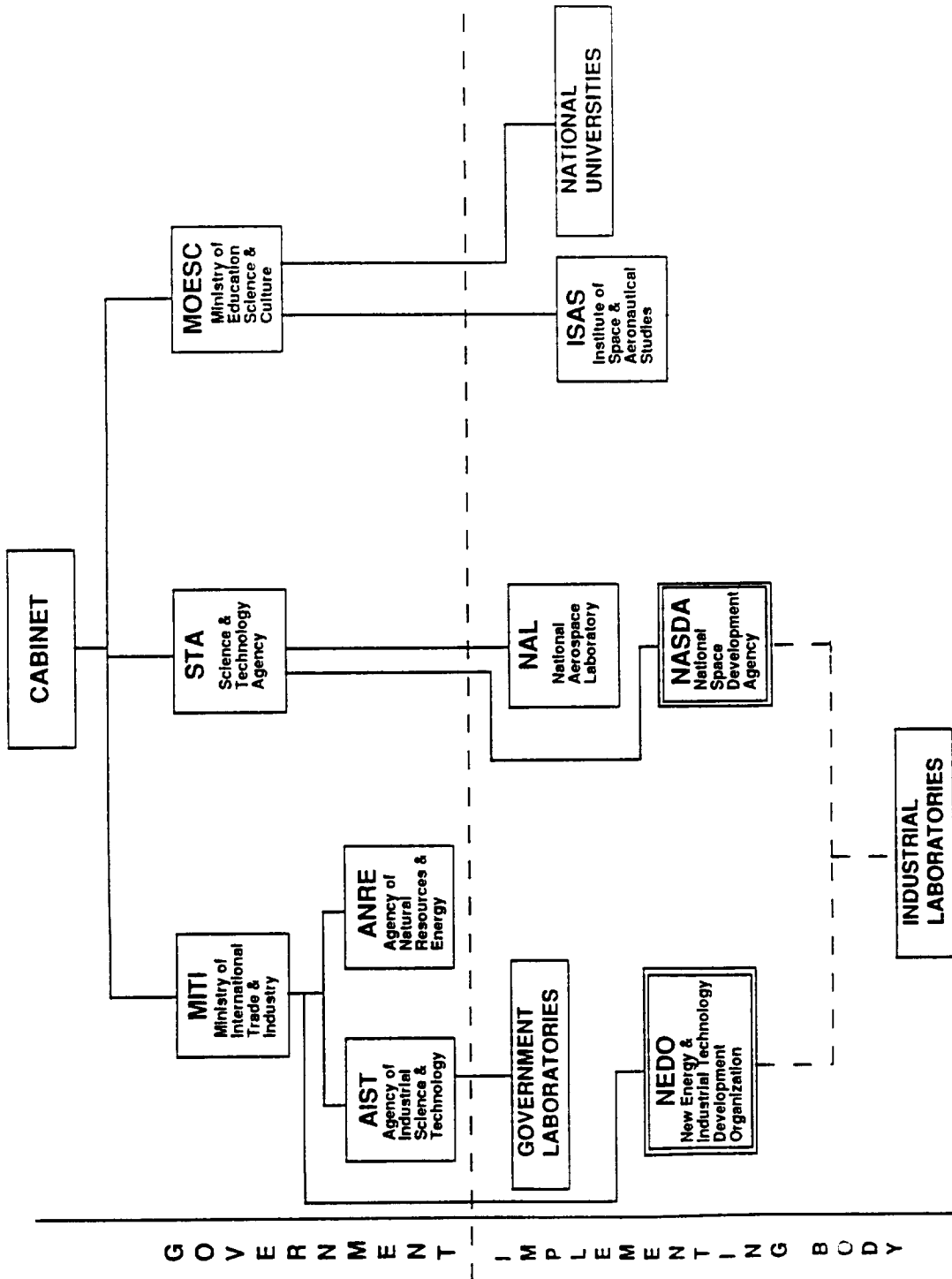


Figure 1.5. Japanese Ministries with R&D Programs in Advanced Composites
(courtesy of Mr. Takeshi Fukumizu, NEDO Washington Office)

Table 1.2
Budget and Personnel for Government Laboratories

Laboratory	Budget (¥M)	Personnel
Natl. Research Lab of Metrology	2111	220
*Mechanical Engineering Lab	3181	279
Natl. Chemical Lab for Industry	3942	356
Fermentation Research Institute	1100	89
Res. Inst. for Polymers & Textiles	1464	126
Geological Survey of Japan	4363	360
Electrotechnical Lab	9332	690
Industrial Products Research Inst.	1360	126
Res. Inst. for Pollution & Resources	3883	324
*Govt. Industrial Lab, Hokkaido	1176	96
*GIRI, Tohoku	523	54
*GIRI, Nagoya	2539	246
*GIRI, Osaka	2551	221
GIRI, Chugoku	667	52
GIRI, Shikoku	486	44
*GIRI, Kyushu	942	91

* Laboratories with programs related to high-temperature advanced composites

Source: Ref. 1.3

There are three major MITI programs which involve high-temperature advanced composites technology:

1. Basic Technologies for Future Industries Project
2. Large-Scale Project
3. Moonlight Project

Under MITI's aegis, the New Energy and Industrial Technology Development Organization (NEDO) has responsibility for implementing the Basic Technologies for Future Industries Project, the Large-Scale Project, and the new Materials for Severe Environments Program, among others. NEDO administers the Research Facility Development Program to build and operate facilities such as the Advanced Materials Research Center that are beyond the means of individual private companies. Finally, NEDO runs the programs on International Cooperation in Research and Development, which have included the "Heat-Resistant Carbon-Ceramic Composite Materials" project with cooperation between DFVLR in Germany and the Kyushu Government Industrial Research Institute (GIRI) in Japan.

Basic Technologies for Future Industries

A number of criteria are considered in selecting the projects for Basic Technologies for Future Industries. These include that the technologies provide a foundation for new industries; that they have a wide impact; that they require long-term research investment that would not be provided by industry; and that they increase "international welfare" by providing technologies attractive to other countries. The programs are funded for eight to twelve years at relatively high levels. Five generic areas are actively funded at present:

1. New materials
2. Biotechnology
3. New functional devices (electronics)
4. High-temperature superconductors
5. Software

In the new materials area, three projects are of interest to this JTEC study. They are the projects for high-performance ceramics, composite materials, and high-performance materials for severe environments, as summarized below.

High-Performance Ceramics. Silicon nitride and silicon carbide monolithic ceramics are being developed for gas turbine components. Although this project has not considered fiber-reinforced composites, much of the technology can serve as a foundation for ceramic matrix composites. The project runs from 1981 to 1992 and was funded at ¥1.1 billion in 1989.

Composite Materials. The goal of this project was to provide composite materials for space and automotive applications. There were three sub-themes:

- a. Fiber-reinforced plastics (FRP) to operate at temperatures less than 250°C with tensile stresses within the fiber of greater than 2.4 GPa at failure
- b. Fiber-reinforced metals (FRM) to operate at temperatures less than 450°C with tensile stresses within the fiber of greater than 1.5 GPa at failure
- c. Materials and design technology required to make and use these materials

No R&D was performed on fibers themselves; the emphasis was placed on the processes for making FRP or FRM using available fibers. The program spanned the years 1981-1988. The objectives were met, and a report on the results was to be issued in February 1990. Though the maximum use temperatures were below

those of interest to the JTEC panel, the fundamental technology developed for these lower temperatures is applicable to higher temperature systems as well.

High-Performance Materials for Severe Environments. In this project initiated in 1989, carbon-carbon composites, intermetallic compounds, and their composites are being developed for a spaceplane and commercial hypersonic transports. The targets for materials behavior have been set for two categories of materials:

- a. Carbon-carbon composites. The maximum use temperature has been set at 1800°C, an ambitious goal. A number of industrial and government laboratories are involved. In general, government laboratories are performing more fundamental studies, while the industrial laboratories are developing processing know-how for complex-shaped, oxidation-resistant carbon-carbon composites.
- b. Intermetallic compounds and their composites. Intermetallic compounds of niobium and molybdenum have been selected to operate at 1800°C; titanium aluminide (TiAl) has been chosen to perform up to 1100°C. The emphasis has been on monolithic materials, but R&D on composite materials is planned for the future. As in the completed composites program, no new fibers will be developed for intermetallics; the program will rely on available fibers such as Nicalon*, silicon carbide or other improved fibers that industry might provide.

The project is scheduled to run from 1989 through 1996. Interestingly, ceramic matrix composites are not part of the project. The High Performance Materials for Severe Environments Project was funded at ¥301 million for 1989. At the time of this Panel's visit, MITI expected to fund the project at ¥1 billion for 1990.

Large-Scale Project

Under the Large-Scale Project, MITI presently funds R&D in eight technologies which are considered to be of importance to the future of Japan. The project on Super/Hypersonic Transport Propulsion was launched in FY1988. This project is designed to provide a highly reliable, efficient propulsion system for a hypersonic, commercial air transport vehicle to be completed in the first decade of the twenty-first century. Materials selection must be made by 1996 to allow construction of the first vehicle. No materials R&D is being performed on this project, as it relies on the results of the High Performance Materials for Severe Environments and other programs. Initial funding for FY1989 was ¥30 million.

* (Nicalon is a trademark of Nippon Carbon Company.)

Moonlight Project

Moonlight projects focus R&D on energy conservation technology; five major research and development areas have been funded since the Moonlight Project was initiated in 1978. Of particular interest is the Ceramic Gas Turbine Project that is scheduled to last from 1988 to 1996. The goal is to apply monolithic ceramics to turbines with an inlet temperature of 1350°C. Although scarcely involving ceramic matrix composites, much of the technology developed would be transferable. This project was funded at ¥675 million in FY1989.

OVERVIEW OF ADVANCED COMPOSITES R&D IN JAPAN

Basic Research

Basic research in high-temperature advanced structural composites is at a much lower level in Japan than in the United States. The panel saw little research effort in the fundamentals which determine the materials system selection or in the fundamentals of composite behavior. The Japanese were familiar with the systems selected for development in the United States and the rest of the world. Similarly, the principles of composite behavior seemed to be well understood, and there are a number of well-known researchers in this area at Japanese universities.

Materials Research and Development

Many Japanese believe that materials research and development provides the foundation for their industries. While the Japanese perform innovative materials research and development, especially in the top industrial and government laboratories, they place special emphasis on processing. In contrast with the situation in the United States, processing studies are not just carried out on a laboratory scale, but also in large pilot plants.

Most noteworthy of the Japanese achievements are those in the development of carbon and silicon carbide fibers. The Japanese lead the world in producing PAN (polyacrylonitrile) and pitch precursor carbon fibers, as well as polymeric precursor silicon carbide fibers. These developments have been largely carried out in industrial laboratories after initial pioneering work in government or university laboratories; the large commercial markets for carbon fibers easily justified the R&D costs. However, some of the Japanese materials producers are realizing now that no large commercial markets exist for many high-temperature advanced structural composites, and they are withdrawing from the market. While carbon, silicon carbide, and some oxide fibers are commercially available, there

does not appear to be any driving force for the production of specialty reinforcing fibers for intermetallic matrices.

The Japanese match the capabilities of the United States in aluminum matrix composites. Especially impressive are applications to automotive engines by Toyota and Honda. Although not truly of the performance level of aerospace metal matrix composites, the serial production of automotive parts allows these manufacturers to proceed down the learning curve in producing low-cost parts.

The Japanese have made rapid progress in developing monolithic titanium aluminides; however, as of this writing they have not yet made fiber-reinforced composites from these or higher melting matrices based on niobium. Silicon carbide fibers are mentioned as potential reinforcements, although they do not appear suitable for these matrices. Alternative fibers are not being considered at present.

Coated and uncoated carbon-carbon composites are some of the materials systems receiving emphasis in the High Performance Materials for Severe Environments Project. Several programs are being funded, and non-project-funded activity at some other industrial and government laboratories is high. The first phase of the program is to match carbon-carbon technology worldwide, then to surpass it. Given the strengths of the Japanese in carbon technology, it is likely that new innovative processes will emerge during the second phase of the program.

OVERVIEW OF ADVANCED COMPOSITES MANUFACTURING IN JAPAN

Manufacturing Philosophy

Advanced aerospace systems will require substantial breakthroughs in the development not only of new materials for extreme environments, but also of new manufacturing methods, processes, and equipment. The simple extrapolation of conventional materials science technology cannot provide the necessary materials systems. Hence, the substantial effort in materials synthesis underway in Japan and described in this report is but the first step in a long process to gain a position in the field of aerospace. If Japan develops the necessary materials science and systems, its entry into and leadership of the future aerospace industry will be assured.

The Japanese manufacturing philosophy in advanced composites, like that in other new fields in which Japanese industry has chosen to enter, calls for the evolutionary development of the role of industry from supplier to partner to leader

by focusing upon those elements of the technology which will differentiate the Japanese products by economics, or by performance, or both.

In the first phase, Japanese industry seeks to serve as a supplier of manufactured components or sub-elements using conventional technology in order for its manufacturing industry to reach the present state-of-the-art. For example, large subcontracting activities at Japanese heavy industry plants are underway in support of Boeing Commercial Airplane Company and McDonnell Douglas. Large-scale structures such as fuselages are manufactured in Japan and shipped to the United States for assembly. (Of course, this practice also occurs in Europe.) The second phase in the philosophy is to partner with leading foreign industries in order to establish a position of parity in systems development (Boeing Commercial Airplane Company had considered joint development of the *TX7* with Japanese industry). Finally, through advances, refinements, and innovations in materials synthesis and fabrication, Japanese industry achieves leadership.

Process Developments

Several process innovations are under development in Japan which promise to impact the field of advanced composites. These include the following:

- * Combustion synthesis
- * Ceramic composites
- * Gas pressure combustion sintering
- * Superplastic ceramics
- * Functionally gradient materials

For metal matrix composites, significant results were reported in which carbon and silicon carbide fibers were combined with aluminum. However, the lack of an end-user industry or application led one chemical company to terminate research in 1988. Unless more commercial applications appear, metal matrix composites R&D in Japan may require active support from the Japanese government, if industry funding decreases.

Manufacturing of High-Temperature Advanced Structural Composites

The manufacturing systems observed during the JTEC panel's visit to Japan were of a conventional level using state-of-the-art process control technology. No evidence was found for use of intelligent control or artificial intelligence in manufacturing. Work in shaping, joining, and machining of advanced composites is either not underway or was not made available to the JTEC panel.

Manufacturing Equipment

Manufacturing equipment development for materials for extreme environments (advanced composites) is at an early stage of development; however, hot isostatic pressing (HIP) facilities of a relatively large scale have been developed. Finally, the largest investment in equipment observed was for the most modern and sophisticated materials characterization equipment. Conventional methods were observed for continuum modeling in solid mechanics, aerodynamics, and heat transfer. No unified program was in place to develop comprehensive models for manufacturing and processing science.

The overall assessment of the study in the area of manufacturing is that the primary work currently focuses on process innovation, with less emphasis on the manufacture of large-scale systems. However, the evidence observed in conventional composites manufacture suggests the potential for success.

Personnel and Facilities

The number of Japanese students entering undergraduate science and engineering programs is decreasing, and at the graduate level the percentage of foreign students is increasing. Contrary to U.S. experience, most foreign students return to their countries of origin after receiving their Ph.D.s in Japan. Many of the personnel in Japanese industrial R&D, except at the top laboratories, have BS or MS levels of education; and the Ph.D.s have frequently received training at foreign universities. In general, materials science and engineering has not progressed as rapidly as in the United States. Many of the materials researchers are from traditional curricula such as chemistry, chemical engineering, and mechanical engineering, as was the case in the United States some years ago.

Teams are usually formed to perform in-depth systematic research. Team solidarity in Japan is high, perhaps because of Japanese culture and/or the more homogeneous education level of the team. By contrast, U.S. research teams often consist of Ph.D.s and two-year community college graduates in the capacity of technicians, and collegial atmosphere in the teams may be lacking. The Japanese industry enjoys the benefits of having relatively well educated, motivated scientists and engineers in jobs not requiring advanced degrees.

The facilities for high-temperature advanced structural composites that the JTEC panel saw varied widely. Large industrial laboratories were generally equipped with state-of-the-art materials characterization equipment; several of the laboratories are unmatched in capability. The facilities of smaller industrial companies, especially those facing strong international competition, were equal to the laboratories of comparable U.S. companies. In general, Japanese companies put their money into equipment, while the physical facilities may be quite spartan.

Government laboratories had varying levels of instrumentation. NAL had a beautiful high-temperature mechanical test facility for composites, while a few government laboratories were poorly equipped. As in the United States, the government laboratories often were well equipped but did not have the support staff to operate the equipment.

Our limited sampling of university research facilities precludes generalizations; however, it is commonly stated that Japanese universities, in general, are poorly equipped. Japan has not yet built a university system to match the research universities in the United States.

SUMMARY

There are a number of observations and conclusions that can be made about the Japanese programs for high-temperature advanced structural composites. There are two drivers for advanced composites in Japan: (1) the national extension of earlier programs on (resin matrix) composite materials and fine ceramics, and (2) their application as an enabling technology for an emerging aerospace industry.

Technically, there is a tendency in Japan to use what materials are available and to emphasize process development, but with no production of hardware. The research and development is roughly broken into three periods over a span of ten years. The first period is largely learning, getting up to speed, and setting intermediate objectives for the second period. During the second period, several parallel approaches per objective may be expected. To an American, this duplication of effort may appear to be inefficient; however, at these early stages, the additional cost is not high, yet the chance for success may be increased greatly. As several of our Japanese hosts stated, "Various paths lead to the top of Mt. Fuji."

The Japanese programs are for development of basic technology, and are not tied to specific systems. The funding is sustained for long periods and the research teams remain together, which means difficult problems can be solved. By contrast, U.S. programs are usually system driven; funding is for shorter periods, and is often interrupted; development teams get broken up; and difficult problems often cannot be attacked.

The High Performance Materials for Severe Environments Project presents the Japanese with a difficulty. Earlier programs were in areas where the technology could lead to large commercial markets. High Performance for Severe Environments may produce enabling technologies for a hypersonic commercial aircraft; however, while hypersonic commercial aircraft may be a large market, the

new materials business may be small and unprofitable. Fortunately for the Japanese, the large vertically integrated Japanese heavy industries may be able to handle this problem better than the U.S. aerospace and materials companies, which are separate entities.

ACKNOWLEDGEMENTS

The members of the JTEC Panel on Advanced Composites would like to thank our Japanese hosts for their efforts to share information with us, especially under the tight schedule set. We are particularly appreciative of the forthrightness of their comments. The level of our success is largely measured by the cooperation of our Japanese hosts.

The panel wishes to thank the JTEC and ISTA staffs (George Gamota, Duane Shelton, Alan Engel, Pat Johnson, Bob Williams, Aminah Batta, and particularly Mr. Geoffrey Holdridge and Kaori Niida) for their supreme efforts and help, and also wishes to thank our sponsors and their representatives (Frank Huband of NSF and Dan Mulville of NASA). The panel members individually are grateful to members of their home institutions who assisted in preparing the various chapters of this report. Finally, we thank JoAnne Margosian of Clemson University for her assistance.

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CHAPTER 2

REINFORCEMENTS: THE KEY TO HIGH-PERFORMANCE COMPOSITE MATERIALS

Salvatore J. Grisaffe

INTRODUCTION

High-temperature reinforcements are the key to high-performance composite materials. Such materials are the critical enabling technological issue in the design and development of twenty-first century aerospace propulsion and power systems. The purpose of this chapter is to review some of the JTEC panel's insights and findings on the status of Japanese fiber and whisker technology and to examine these in light of current U.S. fiber technology.

Conventional materials are too heavy to provide the structural members for future flight systems. Currently the estimated cost of moving one pound to low earth orbit is around \$4,000; cost per pound to the moon is about \$50,000; and cost per pound to Mars is about \$300,000. Thus, the payoff for developing low-density, high-strength fibers and composites for aerospace programs becomes clear.

Figure 2.1 shows how high-performance composites could also generally benefit any future high-speed civil transport aircraft. Oxides of Nitrogen (NO_x) intrusion from combustion and engine noise must be overcome before such an aircraft can be considered feasible. Minimal environmental intrusion is contingent on combustors being able to operate at extremely high temperatures; such combustors must be constructed of, for example, ceramic matrix composites. Minimal airport noise is contingent on exhaust nozzles being very large (using conventional materials they could represent nearly half an engine's weight); such

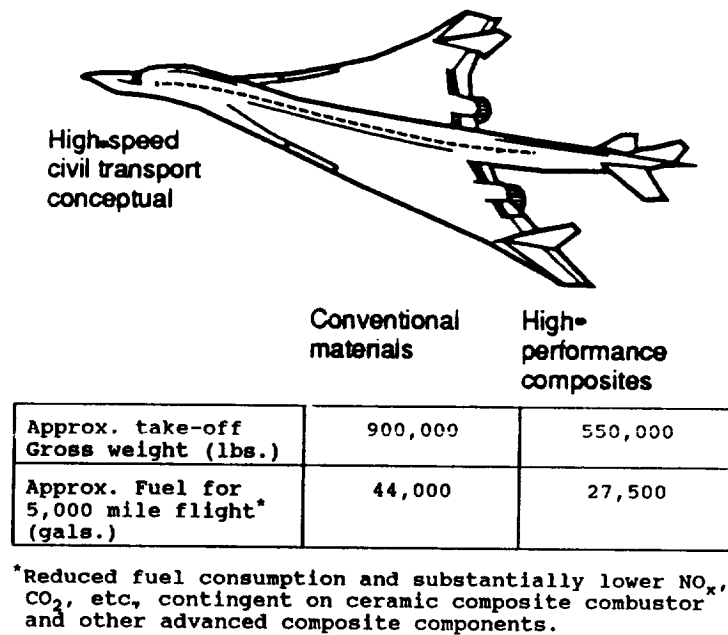


Figure 2.1. The difference in weight and fuel costs between transport built with conventional and with high-performance materials.

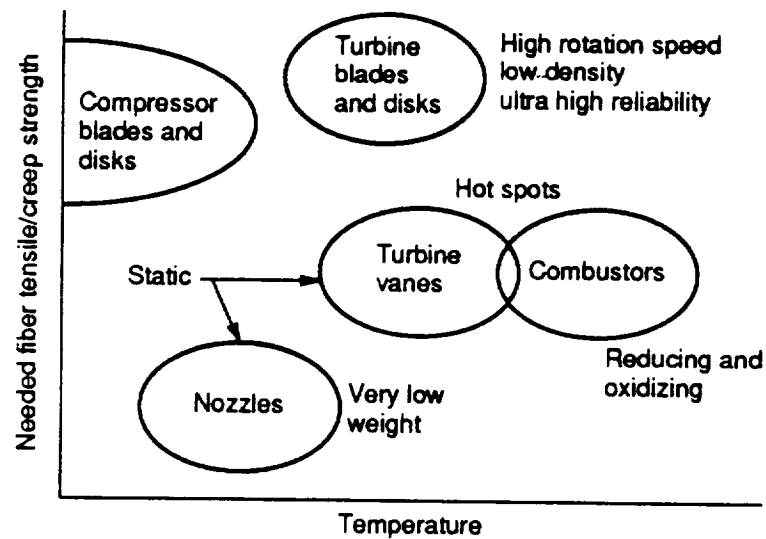


Figure 2.2. Requirements for future aircraft engine components.

nozzles require high-temperature, lightweight intermetallic and ceramic composite structures. In addition, if such composites are used in future high-efficiency engines, lower engine weights will lead to very large reductions in aircraft structural weight. Some estimates approach a 40 percent structural weight reduction compared to conventional materials. These large weight savings could also be translated into more fuel capacity and thus substantial extension in range. This would make trans-Pacific service a viable commercial option for high-speed flights.

The efficiency of the aircraft engines themselves is the final factor in commercial desirability. These engines will operate at extremely high temperatures for substantial fractions of their flight cycle. In addition to the combustor and the nozzle, this means that turbine blades, vanes, and disks, and even the compressor blades and disks will be required to operate at temperatures substantially higher than those of current transport engines (Fig. 2.2). High operating temperatures lead to requirements for high-temperature, high-strength fibers and composites that can resist thermal cycling, creep, and oxidizing environments.

Goals for High-Temperature Fiber Reinforcements

Such aerospace and high speed transport system applications help set high-temperature fiber property goals of low density, high strength and stiffness, and good thermal expansion match with the matrix, as shown in Figure 2.3. According to the rule of mixtures (a first approximation of composite properties based on the contributions of the volume fractions of the fiber and of the matrix), a 50-volume-percent composite of aluminum oxide fibers in a superalloy matrix could, because of its fiber density of only about 4 g/cm³, lower the total density from 8 g/cm³ to 6 g/cm³ and substantially lower rotational stresses as well as the total component weight. More importantly, high strength and stiffness can raise the mechanical properties of composite materials beyond those achievable by today's superalloys and titanium alloys.

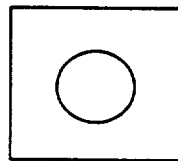
The issue of thermal expansion match between fiber and matrix is a key one. Large differences can result in a wide spectrum of dysfunctional situations. These range from matrix expansion away from the fibers with high temperature and thus minimal load transfer, to very severe thermal ratcheting, which can result in substantial distortion of the composite after repeated thermal cycles. Phase and microstructural stability are particularly important factors for commercial high-speed aircraft engines that must operate near maximum temperature for substantial fractions of their 16000-hour plus life. Phase decomposition, such as the gamma to alpha transition that can occur in aluminum oxide, or the reversible monoclinic to tetragonal transition that occurs in zirconium dioxide, can result in major volume changes as well as significant undesirable changes in properties. Finally, since

- Light weight and low density

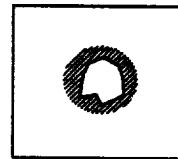
$$\frac{1}{2} \left(\begin{array}{c} \text{Nickel Alloy} \\ 8 \text{ GMS/CC} \end{array} \right) + \frac{1}{2} \left(\begin{array}{c} \text{Aluminum oxide fiber} \\ \sim 4 \text{ GMS/CC} \end{array} \right) = \text{Composite } 6 \text{ GMS/CC}$$

- High strength and stiffness - RT \longrightarrow Maximum use temperature
- Good expansion match with matrix
- Phase and microstructure stability
- Very slow reaction with matrix

Long time
at high
temperature



No reaction



Serious
reaction

Figure 2.3. Fiber goals.

interdiffusion and high-temperature reactions can alter local chemistry, microstructure, and properties--again, usually in a detrimental manner--the thermodynamic stability of the fiber and matrix combination is a key to long-life composites.

Figures 2.4-2.7 show various aspects of the goals for long-life composites. Figure 2.4 shows the density of a number of the compounds of interest as fibers. It also shows the densities of PMC (polymer matrix composites), some of the aluminides (FeAl, NiAl), superalloys, copper, and finally some of the very dense refractory weights of the metals. The lower the density, the lower the weight of and the stresses on rotating components and the lighter the weight of static components.

Figure 2.5 illustrates the various issues that must be considered when discussing fiber strength. First, short-time room temperature tensile strength is, of course, degraded at high temperatures. More critical degradation stems from physical damage to the fibers during fabrication and any matrix reactions that result from the time-temperature exposure related to composite consolidation. Here local flaws, primarily surface in nature, control fiber strength. Second, the long-time, and thus life-controlling issues, are fiber creep (primarily plastic deformation) and the matrix reactions previously discussed. In this case, fiber microstructure controls strength.

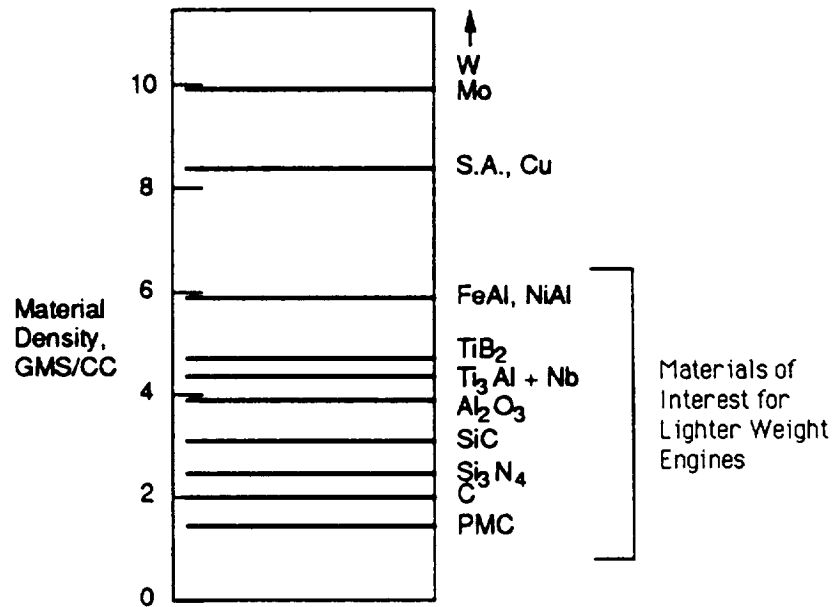


Figure 2.4. Comparative densities of materials used for fiber reinforcement.

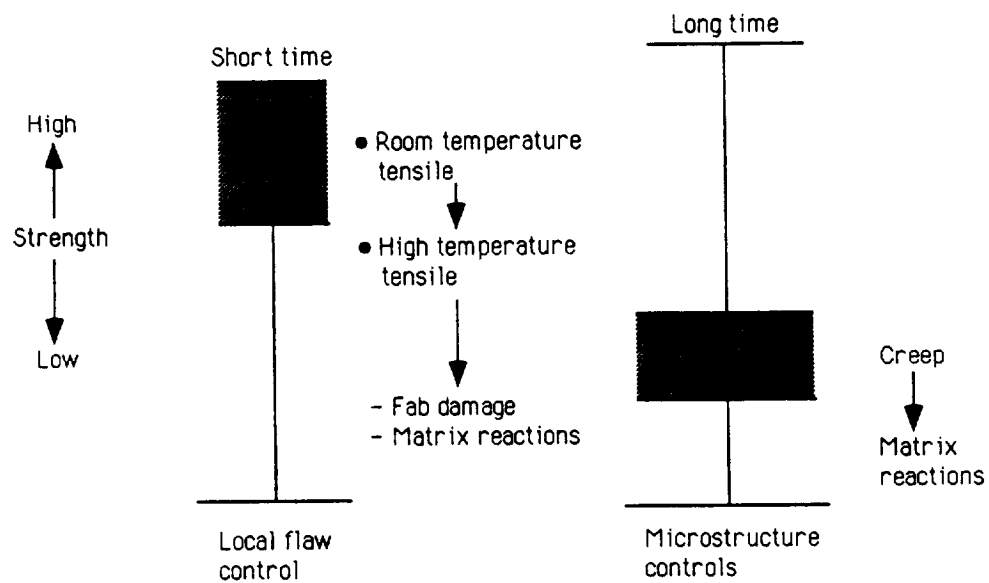


Figure 2.5. Issues affecting fiber strength.

Figure 2.6 presents some coefficients of thermal expansion (CTEs) of a number of the compounds of interest for fiber reinforcements. Because the expansion of a compound or metal is usually not linear, such CTEs are merely an approximation of total behavior. Thus, when thermal mismatch issues are considered, the actual values at any particular temperature must be examined. Finally, Figure 2.7 outlines the methods used to assess the thermodynamic compatibility of a fiber and a matrix. If thermodynamic calculations, based on free energies of formation, indicate that a fiber reacts with or dissolves in a matrix, long term stability of the composite is in question.

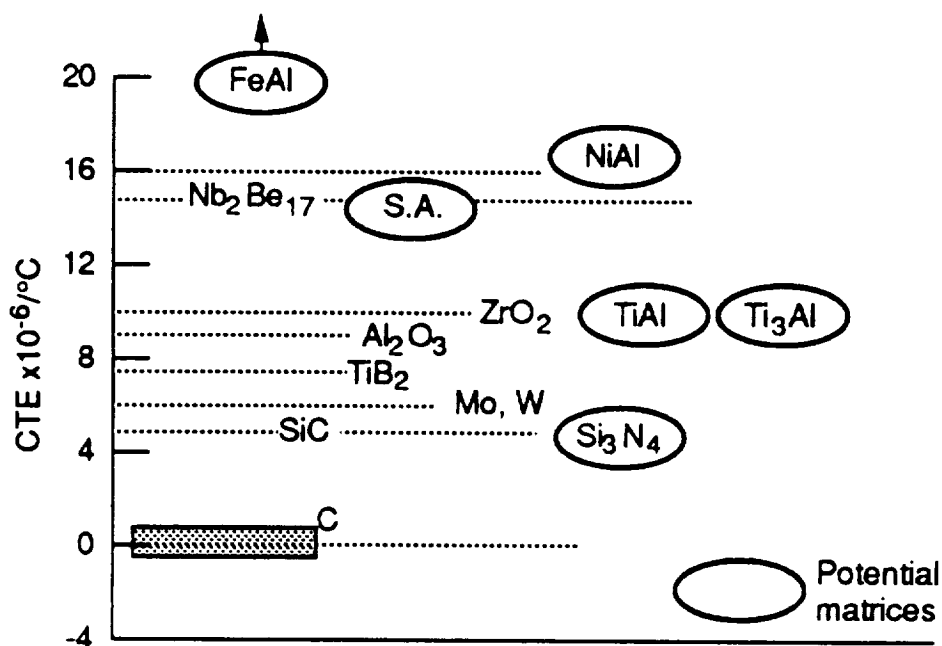
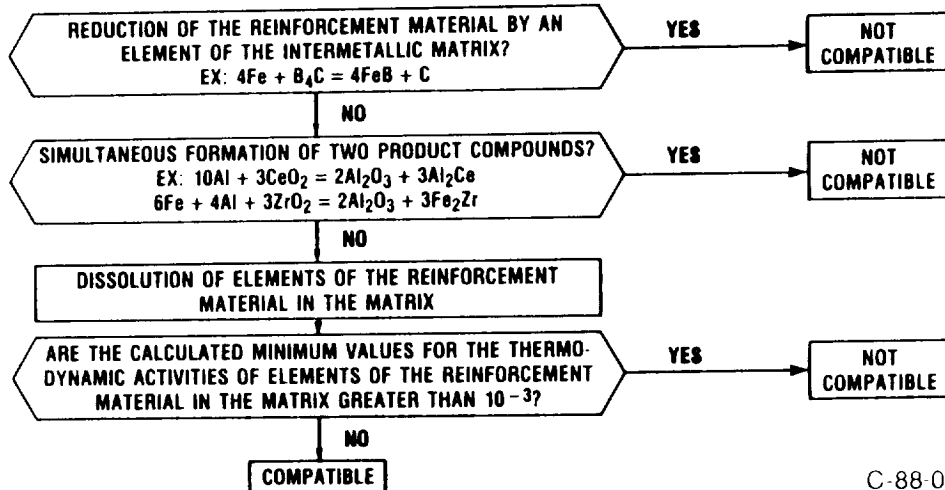


Figure 2.6. Comparative coefficients of thermal expansion.



C-88-08287

Figure 2.7. Methodology of calculations to determine the compatibility of a reinforcement material in a given matrix.

Selection Variables for Fiber Reinforcements

Strength-versus-temperature characteristics. There are currently three major classes of high-temperature, high-performance fibers: carbon fibers, oxide fibers, and fibers of other materials, including intermetallic/interstitial compounds and metals. Figure 2.8 schematically presents the strength-versus-temperature curves for these fiber types. Carbon fibers, as well as fibers of tungsten and molybdenum, react with the oxygen in air to form gaseous and/or weak solid oxides. Such behavior severely limits their use temperature; in an inert atmosphere or vacuum, both carbon and refractory metal fibers have use potential to well above 3000°C . The common oxide fibers, of course, have much better resistance to oxidation because they are already fully oxidized; however, their strength at high temperature is generally only modest unless the fibers are single crystals of the oxide. Currently, the class of fibers with the most promise at high temperatures consists of those compounds that have reasonable--but not outstanding--high-temperature strength and yet have reasonable oxidation resistance as well. In general, most of these fibers consist of very small (and usually stable) grains, although some consist of ultra-small grains or are nearly

amorphous. Some fibers, those that are formed by a chemical vapor deposition process on a small-diameter core fiber, show grain structures that are columnar and perpendicular to the core. And, as previously indicated, some fibers are grown so as to be single crystals.

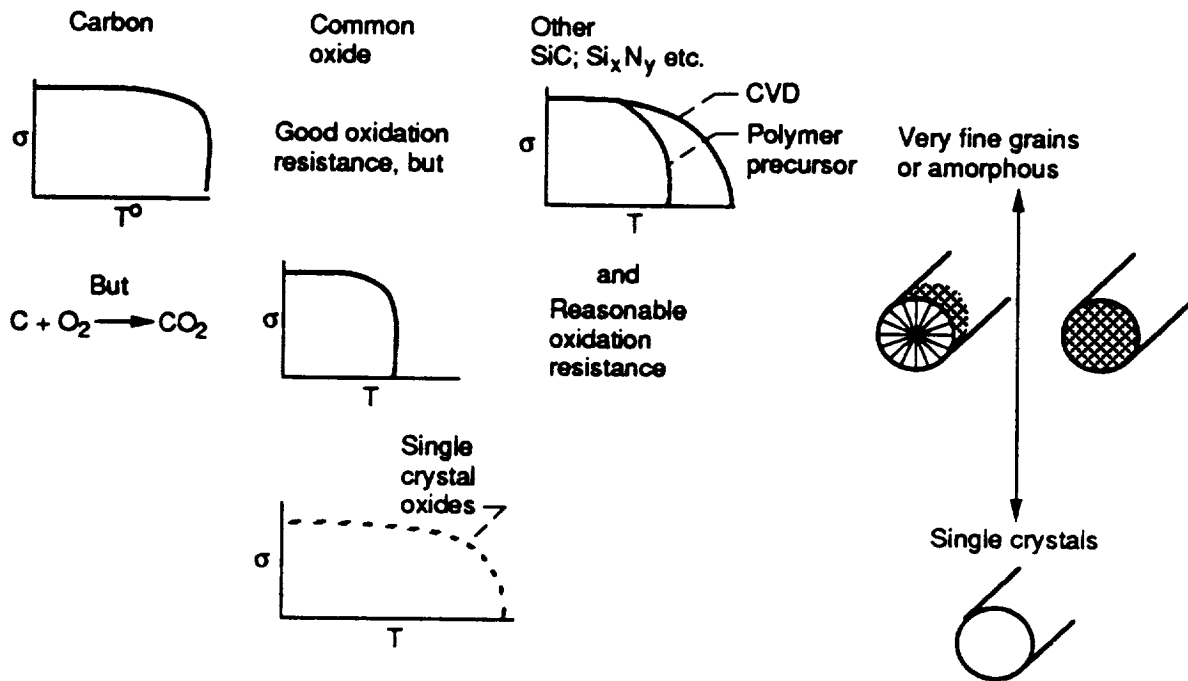


Figure 2.8. Strength-versus-temperature curves for three classes of high-performance fibers.

Fiber processing methods. The preceding discussion shows that the method of fiber processing also provides a way to classify fibers. Figure 2.9(a) presents a variety of schematic representations of fiber production via precursor approaches. In almost every case, a precursor (ranging from selected petroleum pitches to specifically compounded polymers) is forced through a series of tiny orifices to produce some fibrous shape that is then heated, pyrolyzed, or cured to form the fiber. In some cases, additional steps such as heat treatments and stretching-heating are added to achieve the final product. In Figure 2.9(b), a number of direct conversion processes are also schematically displayed. Here molten oxide or polymer materials are forced through small orifices to form fibers. Alternatively, metal rods are extruded and the resulting wire is drawn down to fiber dimensions. Other approaches involve starting with a core fiber as in chemical vapor deposition or with a seed crystal as in melt drawing, laser float zone growing, etc.

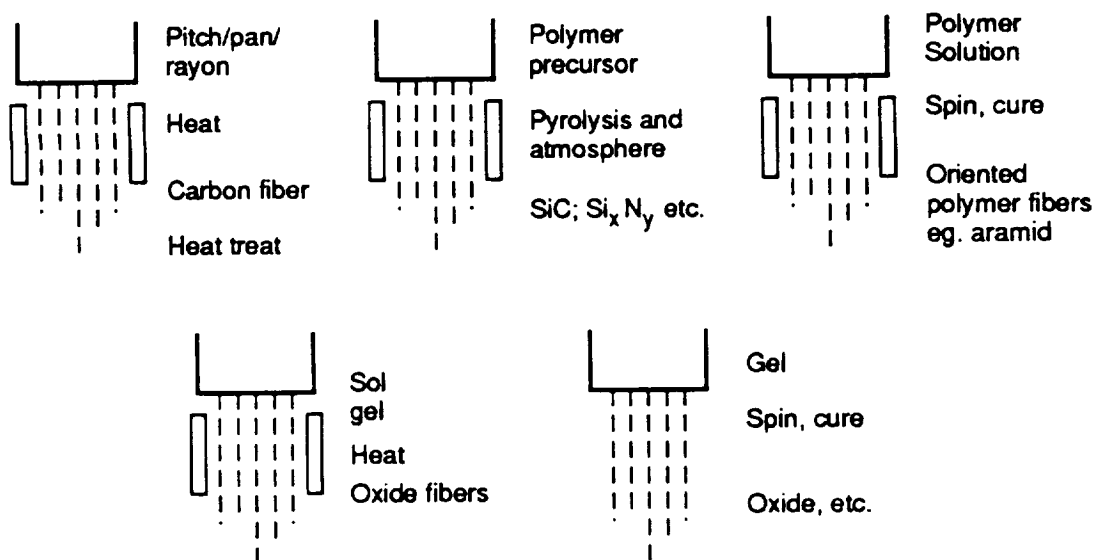


Fig. 2.9(a). Fiber processing via precursors.

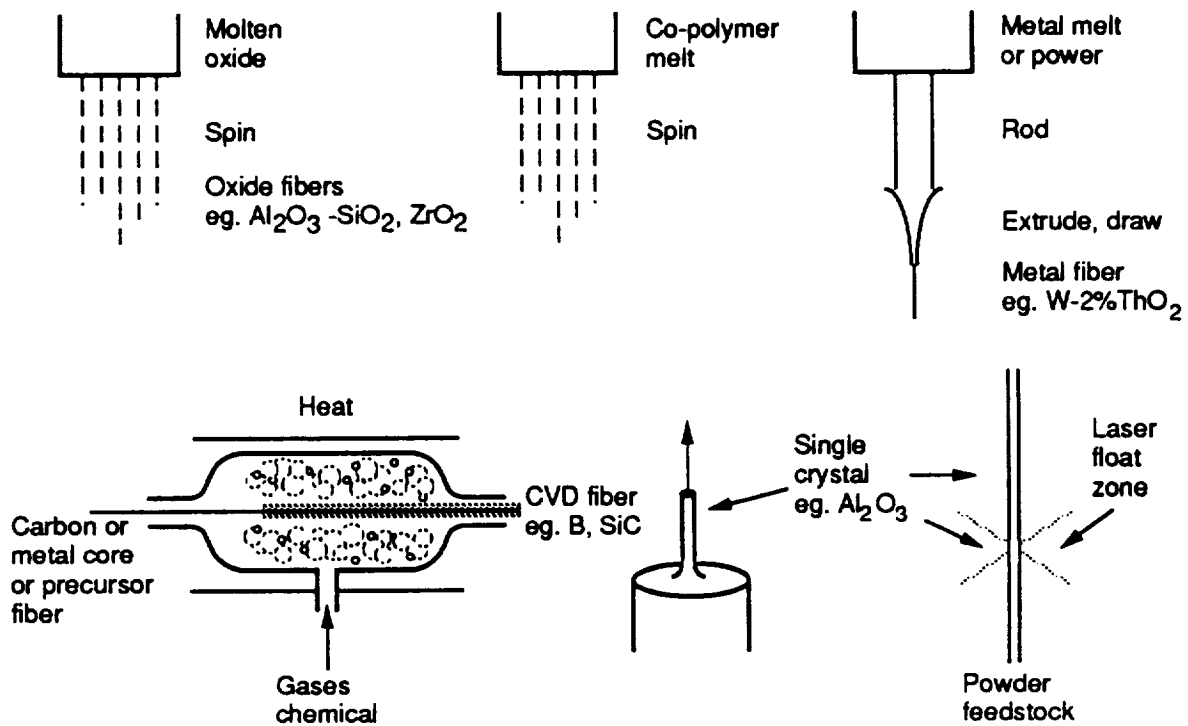


Fig. 2.9(b). Fiber processing via direct conversion.

Fiber diameter. Fibers can also be differentiated based on their diameter. Such differences are shown in Figure 2.10. Generally, large-diameter fibers are incorporated in ductile matrices. In this way the fiber volume fraction can be kept high to exploit the superior properties of the fibers, and yet the spacing between fibers can also be maximized to exploit the inherent ductility of the matrix.

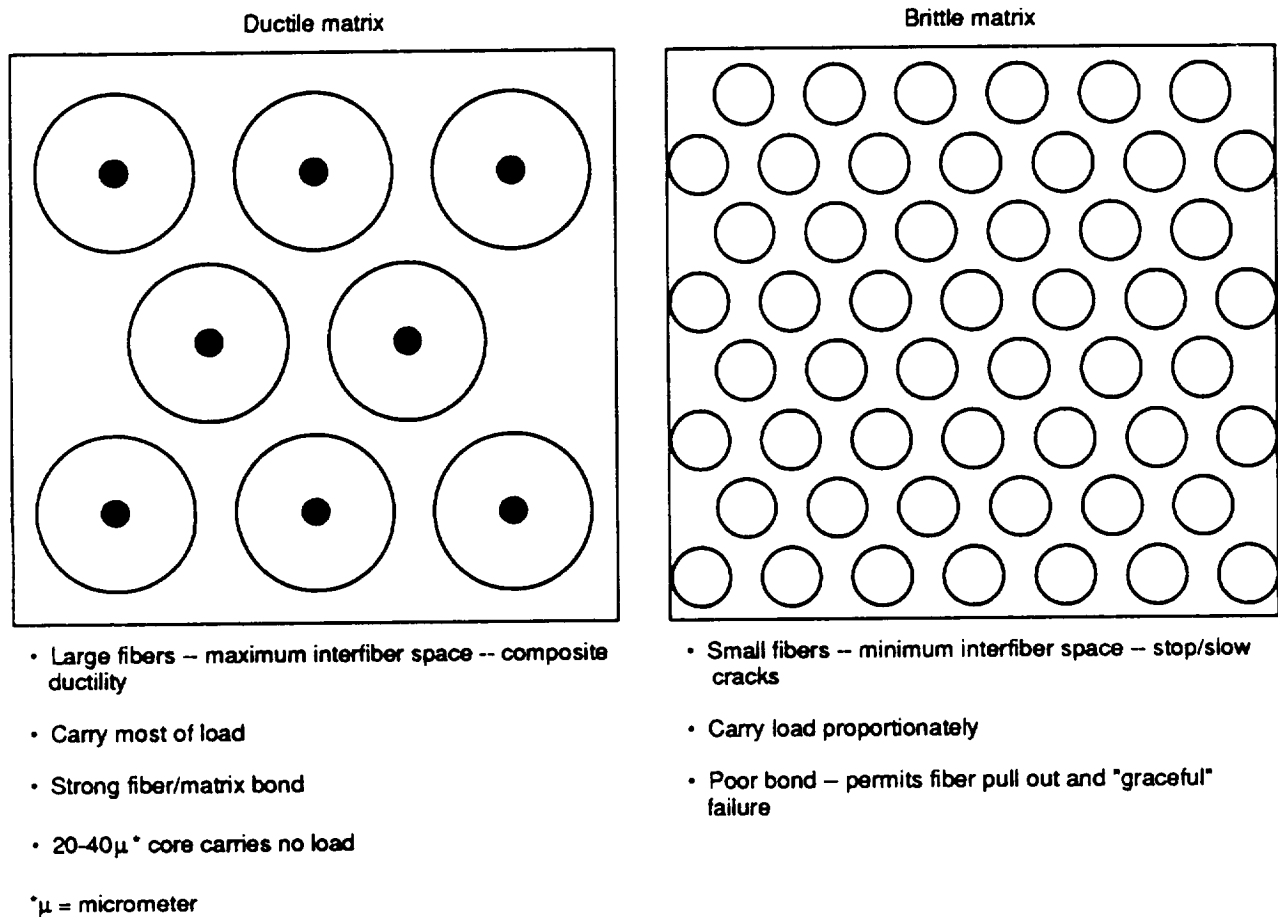


Fig. 2.10. Different diameter fibers for different matrices.

An additional factor is the need for strong fiber-to-matrix bonding so as to transfer load on the matrix to the stronger fibers. In brittle matrices, however, small-diameter fibers are sought, since close fiber spacing is desired to bridge small-process- and service-initiated cracks that could result in catastrophic failure of a loaded ceramic structure. The other issue facing composites consisting of brittle matrices is that the fiber-to-matrix bond should be rather weak, since it is desirable that the cracks deflect around the fibers during matrix fracture ("graceful failure").

Individual versus 2-D and 3-D fiber products. Finally, as shown in Figure 2.11, layups made of individual single fibers are differentiated from composites made from two-dimensional woven cloth as well as from layers of such cloth stitched together into three-dimensional products. The composites consisting of fibers aligned in the same direction as the principal stress exploit fiber strength the most. Angle-plyed monotapes provide off-axis properties. Three-dimensional woven composites show almost uniform but, of course, lower properties in all directions.

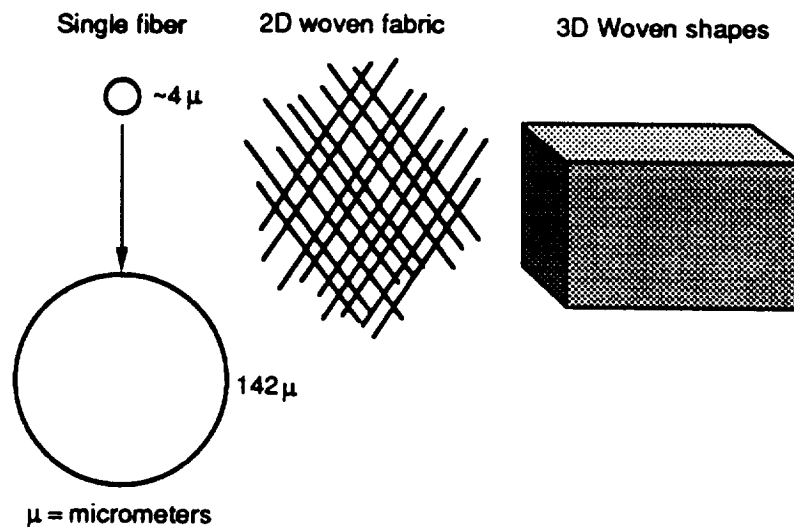


Figure 2.11. From fibers to woven shapes.

Fiber coatings. Generally, fibers are also "sized" or coated with an organic or inorganic material to improve their processability. Figure 2.12 presents some schematic versions of these coatings. In the case of high-temperature fibers, diffusion barriers may be considered to control thermodynamic activity differences and thus minimize interactions with the matrix. Fibers can also be coated to improve their wettability if the fabrication process involves a molten metal, a glass, or a ceramic infiltrant. More recently, coatings have been found to heal surface defects and thus raise the fracture strength of fibers by shifting the failure site from the surface to an internal site (where there are smaller flaws that require higher loads to propagate cracks). In addition, the concept of a relatively thick coating to provide strain accommodation (compliant layer coatings) has been pursued. Such coatings can also offer improved protection to the fiber during fabrication.

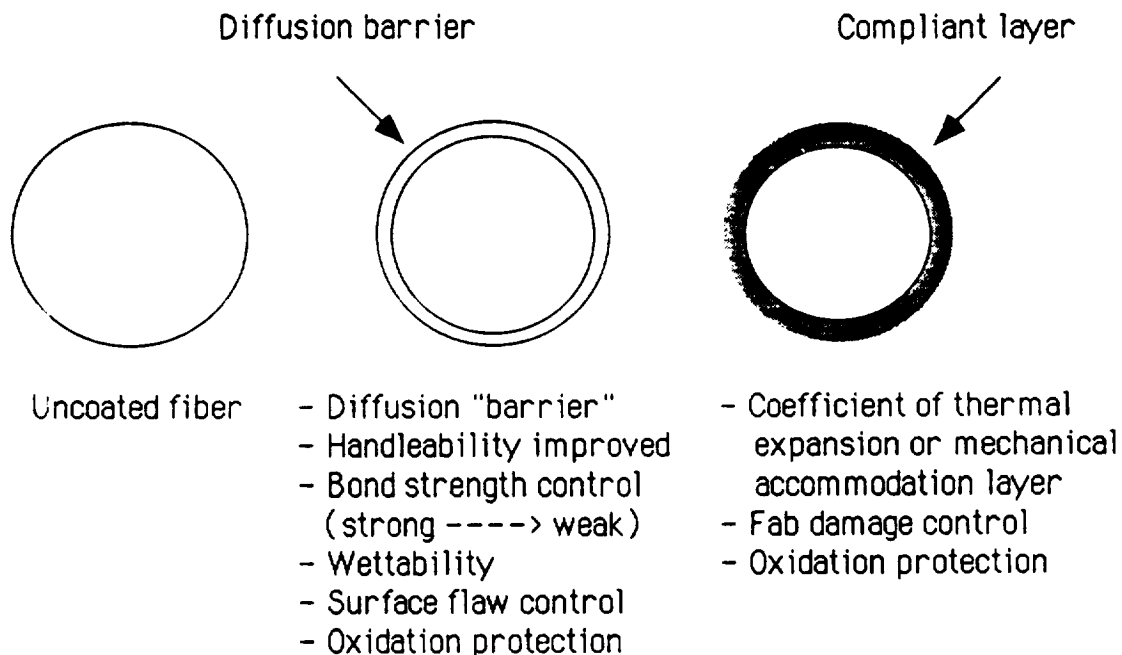


Figure 2.12. Some types of fiber coatings.

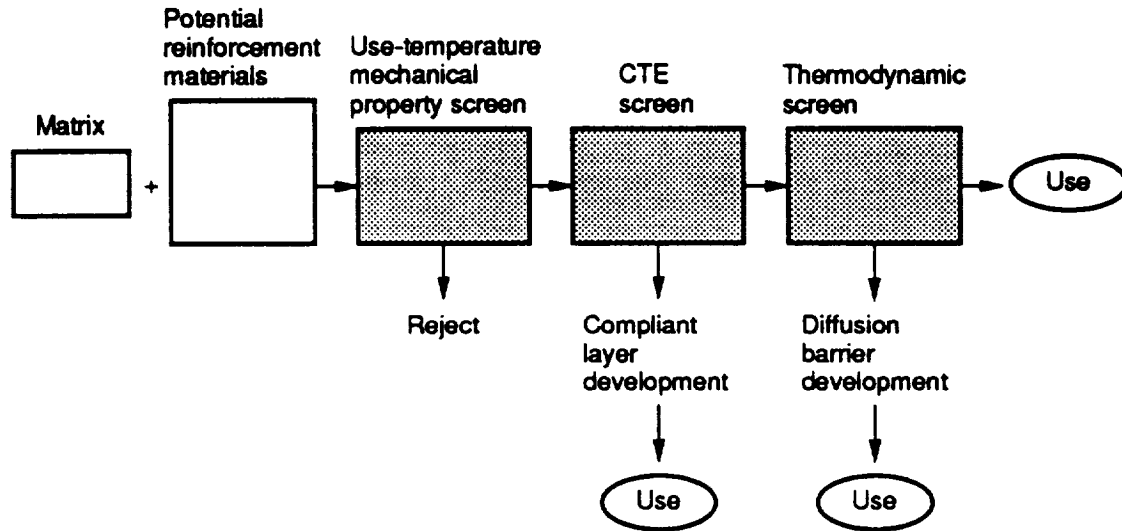


Figure 2.13. Composite screening for eventual use.

An Overall Approach to Composite Selection

Figure 2.13 shows one approach for fiber selection. First, the fiber must have useful high-temperature properties. If it does, then the issue of thermal expansion match can be examined. If a poor match exists, the possibility of using a compliant layer can be explored. For those compositions that pass through both screens, fiber-matrix compatibility must still be considered. If the potential for rapid interdiffusion exists, then a diffusion barrier coating must be considered. Few fibers can pass through all three screens successfully.

Figure 2.14 indicates the amount of fiber that might be needed to make a component. Depending on the fiber diameter and the volume fraction of fiber used in a composite, fiber requirements range from 0.1 to 16 miles for just one cubic inch of material. Thus, fiber production processes must be capable of providing large quantities of continuous fiber. In addition, for fibers with the needed properties, cost typically will be the ultimate factor in fiber selection. As can be seen, except for the very costly single crystal fibers (the cost of which has decreased somewhat recently), fibers can currently be produced at costs that are reasonable for aerospace applications.

For a composite of 50 V/O fiber	Approx. fiber length needed for 1 in. ³ composite, miles	Approx. cost* of fiber in 1 in. ³ composite
<ul style="list-style-type: none"> • Al₂O₃ monocrystal (250 μ ** dia.) 	0.1	\$7,500
<ul style="list-style-type: none"> • SiC CVD (142 μ ** dia.) 	0.3	\$ 132
<ul style="list-style-type: none"> • Al₂O₃ PP (250 μ ** dia.) 	~16	\$ 30
<ul style="list-style-type: none"> • SiC PP (250 μ ** dia.) 	~16	\$ 26

* Cost values after Hillig (See chapter 3)

** μ = micrometers

Figure 2.14. A rough estimate of fiber length requirements and costs for a 1-in³ composite.

FIBERS NOW AVAILABLE IN THE UNITED STATES AND JAPAN

Silicon carbide-based fibers. Table 2.1 lists the commercial and experimental silicon carbide-based fibers available in the United States and Japan. Note that the Japanese fibers Nicalon (15 micrometers or μm in diameter) and Tyranno (9 to 11 μm in diameter) are available from U.S. distributors Dow Corning and Textron, respectively, both fiber manufacturers themselves. Nicalon and Tyranno fibers are derived from polymer precursors.

Table 2.1
SiC Fibers Available in the U.S. and Japan

(a) United States

Fiber	Company/University
Nicalon ^a (Si-C-O)	Dow Corning (U.S. distributor for Nippon Carbon)
Tyranno ^a (Si-Ti-C-O)	Textron (U.S. distributor for UBE)
SCS-2,6,9,10 ^c (carbon core, 142-um diam)	Textron
Experimental ^{a,b} (10-um diam)	Dow Corning
Experimental ^{b,c} (15-um diam, 7-um carbon core/tow)	SUNY
Experimental ^c	RPI

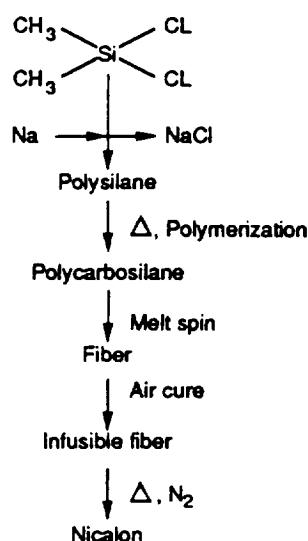
(b) Japan

Fiber	Company/University
Nicalon ^a (Si-C-O) 14-um diam: NL-200 (ceramic grade) NL-400 NL-600	Nippon Carbon
Tyranno ^a (Si-Ti-C-O, 9- to 11-um diam)	UBE

^aDerived from polymer precursor.^bResearch and development effort supported by NASA Lewis.^cProduced by chemical vapor deposition.

Textron's SCS family of fibers is produced by chemical vapor deposition onto a carbon core and are much larger in diameter (75 and 142 μm) than the Nicalon and Tyranno fibers. SCS fibers are available with a variety of surface coatings in order to tailor the interface to the selected matrix material. Dow Corning is exploring a small (10 μm) diameter SiC fiber from a polymer precursor under sponsorship of NASA Lewis Research Center. Likewise, NASA Lewis is sponsoring research at the State University of New York at Buffalo to develop a 15- μm -diameter SiC fiber produced by chemical vapor deposition. Similar work is also being conducted at Rensselaer Polytechnic Institute.

Figure 2.15 is an extraction of Nippon Carbon Company, Ltd. literature and shows the polymer precursor and fiber production steps as well as some company information on the Nicalon finished products. Table 2.2 lists some literature values for key Nicalon fiber properties. This material is available in a variety of yarns, woven cloth, rope, paper, mat, etc.



* μ = micrometers

Finished products of Nicalon®.



- Continuous fiber (multi-filament)
- Chopped
- Various woven products (cloth, braid, tape, rope)
- Various composite materials (MMC, PMC, CMC)

Products code number of Nicalon® continuous fiber.

Nicalon® (Silicon Carbide Continuous Fiber) is available in the following types designed for various applications.

type { NL - 200 series
NL - 300 series
NL - 400 series

Depending on the application of Nicalon® a suitable sizing agent can be chosen.

Product code number	Type of sizing agent
NL - XX0	NONE
NL - XX1	Use in PMC(epoxy)
NL - XX2	Use in MMC, CMC
NL - XX3	Use in PMC(BLMI)

12 and 15 μ * fibers (continuous)
500 filament tows
~24,000 lbs./yr.
(24x10⁶ miles/yr.)

Figure 2.15. Nicalon SiC fiber (extracts from Nippon Carbon Co., Ltd. brochures).

Table 2.2. Reported Properties of Nicalon Fibers

Density, ρ , g/cm ³	2.6
Tensile strength, GPa	2.5-3
Modulus of elasticity, E, GPa	180-200
Coefficient of thermal expansion, CTE, 10 ⁻⁶ /°C	3.1
Maximum use temperature, °C	1200

Silicon nitride-based fibers. Table 2.3 lists the commercial and experimental silicon nitride-based fibers available in the United States and Japan. Both the United States (because of the Dow Corning fibers identified as HPZ and MPDZ) and Japan (because of Tonen's silicon nitride and the new silicon boronitride fibers) have such fibers. Furthermore, since Mobil and Exxon each own 25 percent of Tonen, there is some U.S. commercial involvement in all silicon nitride-based fibers.

Table 2.3
Silicon Nitride Fibers
Available in the U.S. and Japan

(a) United States

Fiber	Company
HPZ ^a (8- to 15- μ m diam)	Dow Corning
MPDZ ^a (10- to 20- μ m diam)	Dow Corning
SiN ^a	Tonen ^b
SiNB ^a	Tonen ^b

(b) Japan

Fiber	Company
SiN ^a (10- μ m diam)	Tonen ^b
SiNB ^a	Tonen ^b

^aDerived from polymer precursor.

^bOwnership, 25 percent Mobil and 25 percent Exxon.

Figure 2.16 is a compilation of information and pictures from Tonen's literature. It shows the fiber production process--fiber spinning and final product (enlarged view). Figure 2.17 shows the process described by Tonen to produce its new silicon boronitride fiber, which was stated to be amorphous to 1700°C and to have an elastic modulus of about 200 GPa (only data provided). Although the Tonen fiber is viewed as developmental, Figure 2.18 shows some property data that indicate the need to maintain low amounts of excess silicon to prevent crystallization of the normally amorphous fiber, and show that the use temperature of this fiber is no more than 1100°C .

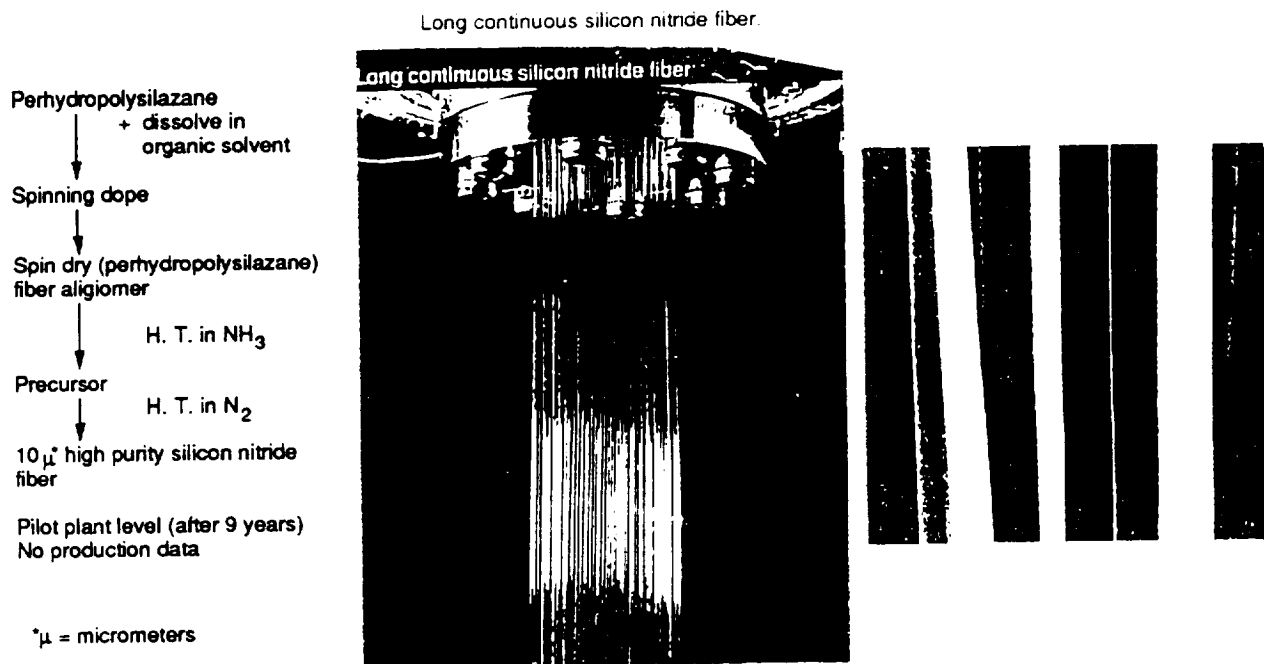


Figure 2.16. Tonen silicon nitride fiber (extracts from Tonen Corp. brochure).

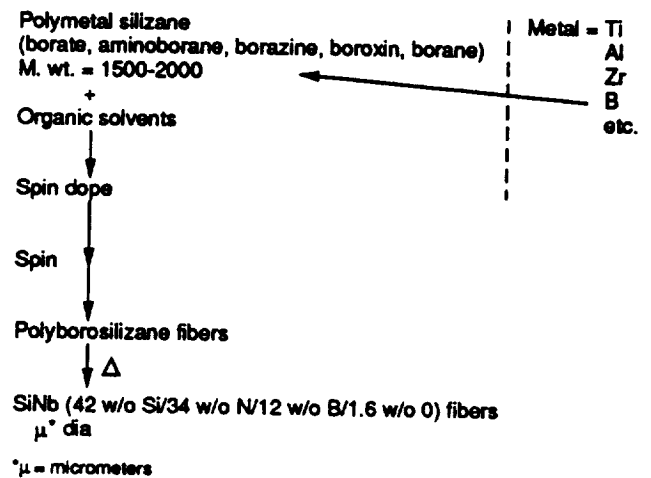


Figure 2.17. Production process for new Tonen SiNB fiber
of Tonen Corp., U.S. patent 4,886,860 (12/12/89).

Typical properties of silicon nitride fiber

Tensile strength	360 ksi (2.5 GPa)
Tensile modulus	36 msi (250 GPa)
Density	2.5 g/cc
Filament diameter	10 μm^*
Coef. of thermal Exp.	$1.5 \times 10^{-6}/^\circ\text{C}$ (up to 800 $^\circ\text{C}$)
Crystal structure	Amorphous
Cont. use temperature	1200 ($^\circ\text{C}$)
Composition (%)	Si, N, O, H, Si/N = 0.75-1.25 O < 1.0%

Typical properties of perhydropolysilazane

Number average molecular weight	500-4000
Ceramic Yield (to 1500 $^\circ\text{C}$)	85-93 wt%
Form	Liquid-solid
Solubility	Organic solvent
Composition	Si, N, O, H, Si/N = 0.75-1.25 O < 1.0%

If excess $\text{Si}/\text{Si}_3\text{N}_4$:

0.47: α SiN to 1400 $^\circ\text{C}$ some β Si_3N_4 at 1500 $^\circ\text{C}$

0.01: amorphous to 1400 $^\circ\text{C}$ small Si, α , β at 1500 $^\circ\text{C}$

* μ = micrometers

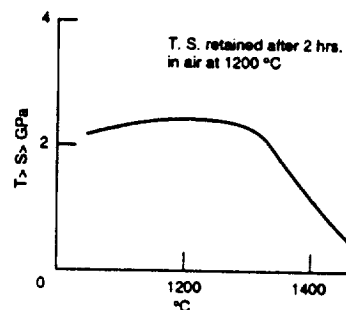


Figure 2.18. Properties of Tonen SiN fiber (extracts from Tonen Corp. brochures).

Oxide-based fibers. Table 2.4 lists the commercial and experimental oxide-based fibers available in the United States and Japan. It is interesting to note the large number of oxide fibers produced in the United States. Even Altex by Sumitomo Chemical is available from Textron, its U.S. distributor. Most of the fibers listed are produced either from polymeric precursors or from a sol-gel or slurry process. The Saphikon fiber (250 μm diameter) is, however, produced by melt extraction, and the NASA Lewis experimental fiber is made by a laser float zone (LFZ) process. The latter two fibers are between 100 and 250 μm in diameter, but most of the oxide fibers fall in the range 10 to 30 μm .

Table 2.4
Oxide Fibers Available in the U.S. and Japan

(a) United States

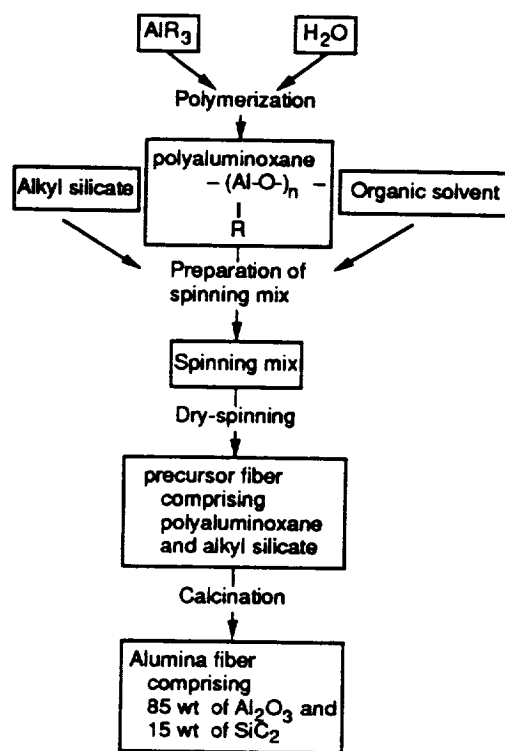
Fiber	Company
Altex ^a (Al ₂ O ₃ -15SiO ₂)	Textron (U.S. distribution)
Saphikon (Al ₂ O ₃ mono-crystal, 250- μm diam)	Saphikon
Nextel (10- to 12- μm diam):	3M
312 (glass SiO ₂ -Al ₂ O ₃ -B ₂ O ₃)	
440 (glass SiO ₂ -Al ₂ O ₃ -B ₂ O ₃)	
480 (glass SiO ₂ -Al ₂ O ₃ -B ₂ O ₃)	
Z-11 (ZrO ₂ /SiO ₂ /Al ₂ O ₃)	
PRD-166(Al ₂ O ₃ -ZrO ₂ , 20- μm -diam, slurry)	Dupont
FP(Al ₂ O ₃ , 20- μm diam, slurry)	Dupont
Experimental (Al ₂ O ₃ , 100- to 200- μm diam, LFZ)	NASA Lewis
Experimental (Al ₂ O ₃ , 25- to 50- μm diam, polyxyl)	3M; Dupont
ZYT(ZrO ₂ , 3- to 6- μm diam)	Zircar

(b) Japan

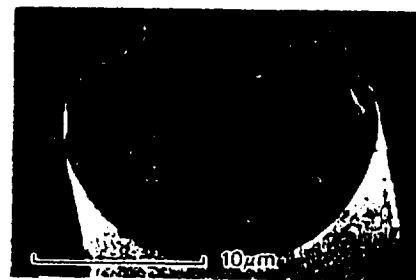
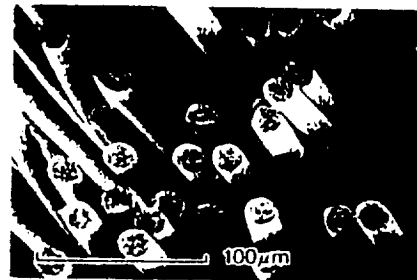
Fiber	Company
Altex ^a (Al ₂ O ₃ -15SiO ₂ , 10- and 15- μm diam)	Sumito Chemical Company

^aDerived from polymer precursor.

Figure 2.19 is a compilation of Sumitomo literature showing the polymer precursor process used to achieve its Altex gamma alumina fiber and showing the very small grain sizes that are achieved. Figure 2.20 is a second compilation of the Sumitomo literature showing some of the mechanical property data. The reason for the fiber's useful limit being around 1100°C is the decomposition of the silica-rich gamma alumina to alpha alumina and mullite at that temperature. The Altex fiber is also available in a variety of forms, including rovings and woven (plain and satin) materials.



10 and 15 μ * fibers (continuous)
500 and 1000 Filament tows (10 μ -1000 only)
20,00 lbs/yr (14x10⁶ miles)
* μ = micrometers

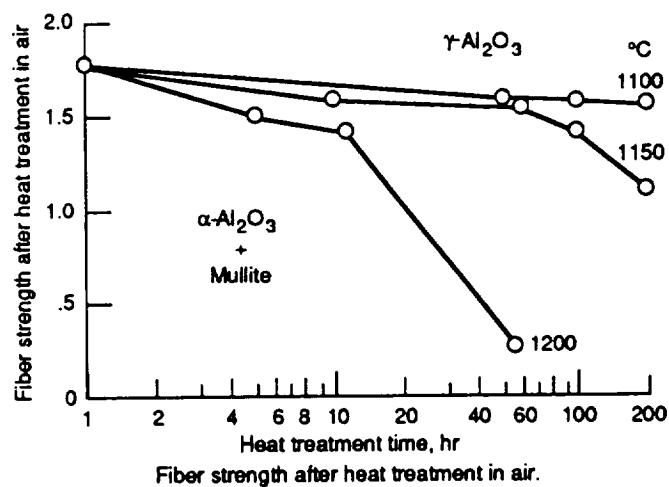


Scanning electron micrograph of "Altex".



Transmission electronmicrograph of "Altex".

Figure 2.19. Polymer precursor process for Altex alumina fiber of Sumitomo Chemical, U.S. patent 4,101,615 (7/18/78) (extracts from Sumitomo brochures).



Properties of "Altex"

Chemical composition		
Al ₂ O ₃	(wt.)	85
SiO ₂	(wt.)	15
Impurity	(wt.)	<0.05
Crystal phase		γ-Alumina
Density	(g/cm ³)	3.3
Diameter	(μm)	10, 15
Filaments/yarn		500, 1000
Tensile strength	(GPa)	1.8
Tensile modulus	(GPa)	210
Maximum use temperature	(°C)	1,100*
Appearance		Colorless and transparent
Refractivity index (No ²⁰)		1.67

* Temperature below which strength retention is higher than 90% for long period of time.

Figure 2.20. Properties of Altex alumina fiber
(extracts from Sumitomo brochures).

Other fibers. As shown in Table 2.5, a number of other fibers are being developed or are available commercially. In general, however, the few fibers of this nature that we came across in Japan were identified with universities, and thus may be farther from commercial production.

Table 2.8
Other Fibers Available in the U.S. and Japan

(a) United States

Fiber	Company/ University
$Nb_2Be_{17}^{a,b}$ (125- to 250- μ m diam)	Textron
$CrB_2^{a,b}$ (125- to 250- μ m diam)	P&W
Ti_xAlC (Mo core, 200- μ m diam)	Textron
CrB_2^b (125- to 250- μ m diam)	SUNY
HfN	Ultramet
TiC	Ultramet
B/BN	Ultramet
TiB_2^b (Mo core, 70- μ m diam)	SUNY
TiB_2^b (Mo core)	Amercom
TiB_2^b (Mo core, 65- μ m diam)	RCI

(b) Japan

Fiber	Company/ University
$BaTiO_3$ (5- to 10- μ m long)	Kyoto University
B or B_4C	Tokyo University (Dr. Okura)

^aResearch and development effort supported by
 NASA Lewis.

^bProduced by chemical vapor deposition.

Carbon fibers. A large number of carbon fibers are produced in the United States as well as in Japan. Table 2.6 lists some (but not all) of the experimental and commercial carbon fibers available in the United States and Japan. They can be differentiated by their starting material--either a wide range of petroleum pitches or polyacrylonitrile (PAN). One class of pitch-derived fibers consists of general purpose (GP) pitch fibers, which are usually short and of lower strength. A second class of pitch fibers consists of a variety of high-performance, high-strength fibers. These are further differentiated by the terms HT (high tensile strength), HM (high modulus), and UHM (ultrahigh modulus).

Table 2.6
Some Carbon Fibers Available in the U.S. and Japan

(a) United States

Fiber	Company
Magnamite ^a (Multiple variations: HMS,HMU,AS1,AS2,AS4,AS6, IM6,HTS)	Hercules
HDG	Fiber Materials, Inc.
Microfil 40	Fiber Materials, Inc.
Microfil 55	Fiber Materials, Inc.
Celion-base structural materials ^a (GY-80, 1000, 3000, 6000, 12 000)	May be Japanese- manufactured
Torayca	Amoco (licensee)
Panex (30, 30Y/3000, 300Y/8000, 30R)	Stackpole
Fortafil ^a (3(C),3(O)5(O), OPF(C),OPF(O))	Great Lakes Carbon
Thornel ^a (T-40,T-50,75, T-300,400,T-500,700)	Amoco
PAN-50 ^a	Amoco
VSA-11 ^b (VS-0032)	Amoco
P-VSB-32	Amoco
P-VS-0053 ^c	Amoco
Grafil (IMS, HM-S/10K, HMS/6K, XA-S)	Hysol Grafil Co.
Hitex ^a	Hitco Materials, Inc.
Hispan ^a	Hercules (ownership, 50 percent Sumitomo)
Experimental ^c	Dupont
Experimental ^c	Amoco

^aPolyarilonitrile-based.

^bMesopitch-based.

^cPitch-based.

^dPitch precursor; Cherry process.

Table 2.6--Continued

(b) Japan

Fiber	Company
Petroka ^a (HM50, HM60, HM70)	Kashima Oil
Petroka ^b (20- μ m diam, core for CVD)	Kashima Oil
Granoc ^c (XN-40, XN-50, XN-70)	Nippon Oil
Torayca ^a (T-400, T-400H, T-800, T-1000, M-30, M-40, M-40J, M-46, M-46J, M-50)	Toray Industries (U.S. licensee, Amoco)
Besfight ^a (ST-2, ST-3, IM-400, IM-600, HTA, HM35, HM40, HM45)	Toho Rayon Ltd.
Pyrofil ^a (T-1, T-3, MM-1, LM-2, LM-5, HM-2, SM-1)	Mitsubishi Rayon
Donacarb ^d (F, S) F-140 (short and long) F-500 F-600	Osaka Gas Co.
Experimental ^c (short fibers)	Kureha Chemical
Forca ^c (FT 700, FT 500, UHM Tonen, HM, HT; 10- μ m diam.)	Tonen
Hispan ^a	Sumitomo
Experimental ^c	Ueda
Carbalonz ^a	Nippon Carbon

^aPolyarilonitrile-based.^bMesopitch-based.^cPitch-based.^dPitch precursor; Cherry process.

Japan produces over 5,000 tons of carbon fiber per year but uses only about half that amount for its own products. The Japanese have not only developed the PAN approach but have a strong capability in pitch-based fibers. For example, Granoc is a Nippon Oil Company, Ltd. product involving a 10- μ m-diameter pitch-based fiber. Nippon Oil reported production capacity up to 50 tons/year from its Yokohama plant. Figure 2.21 shows some of the forms in which Nippon Oil Company, Ltd. Granoc fiber is available from Nippon Oil Company, Ltd. and some of the applications for the fiber; Figure 2.22 shows some mechanical properties of Granoc based on data extracted from Nippon Oil Company, Ltd. literature.

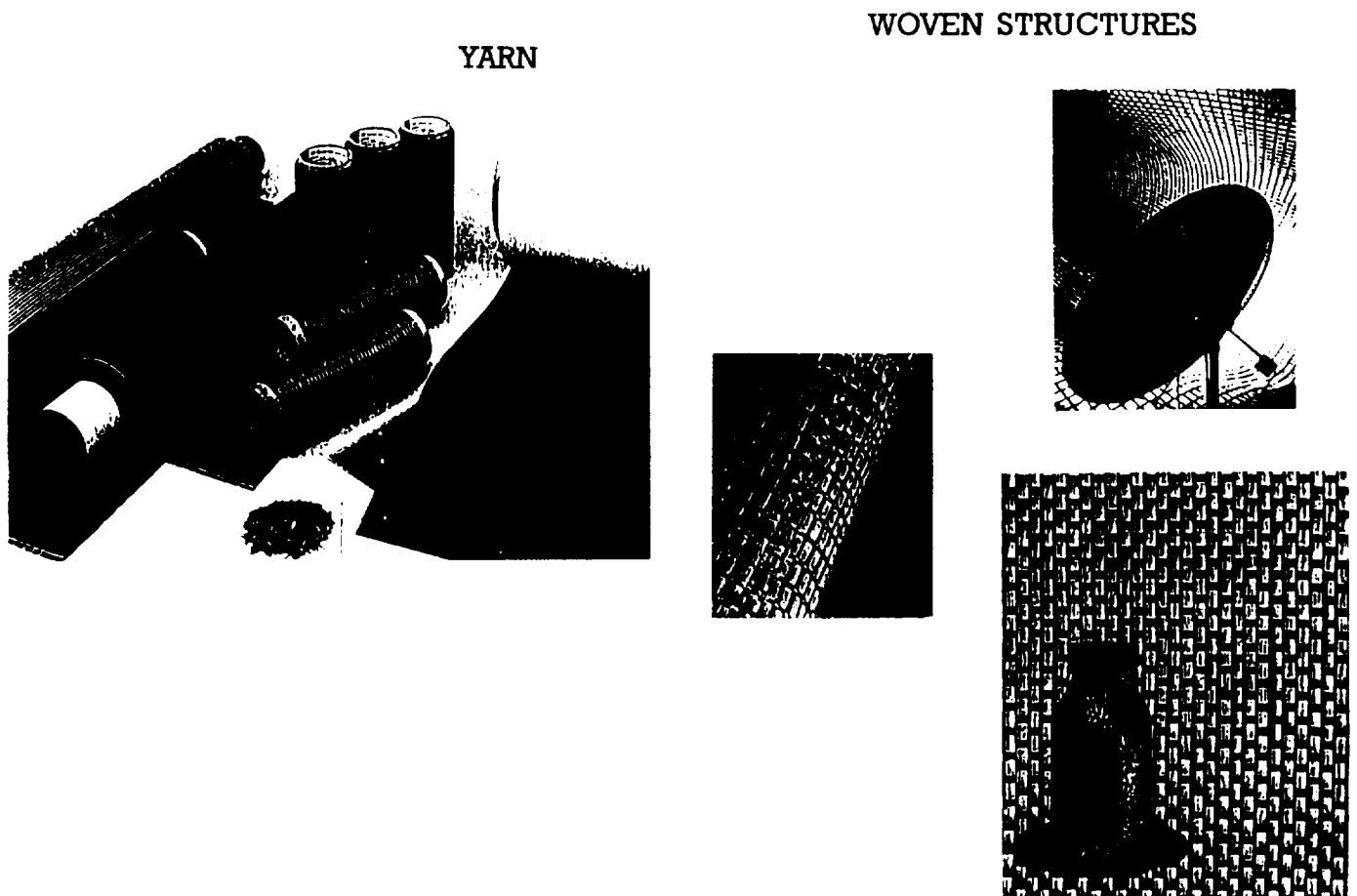
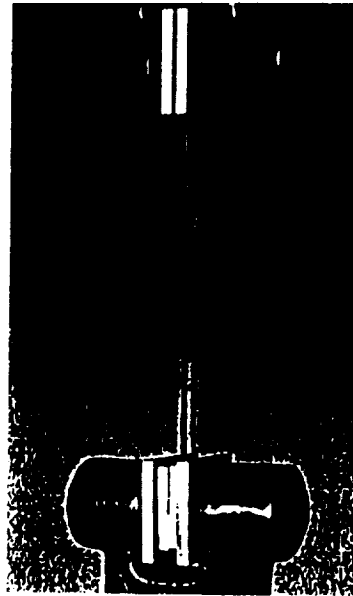
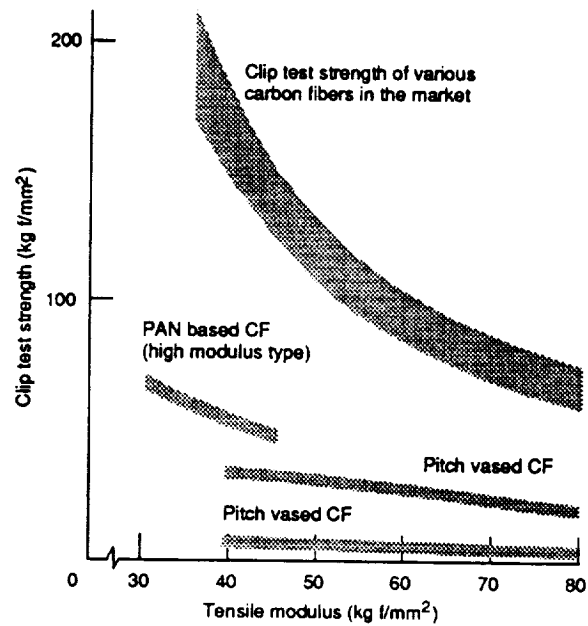


Figure 2.21. Some forms and applications of Granoc fiber
(extracts from Nippon Oil Co., Ltd. brochures).



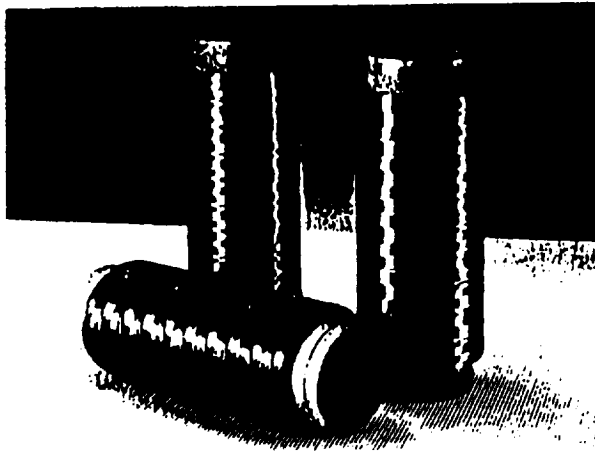
GRANOC fiber Nippon oil.



GRANOC mechanical properties	Special grades available for Aerospace use		
	XN-40	XN-50	XN-70
Modulus (10^3 kg l/mm ²)	40	50	70
Strength (kg l/mm ²)	330	330	340
Elongation at failure (%)	0.83	0.66	0.49

Figure 2.22. Typical properties of Granoc carbon fiber
(extracts from Nippon Oil Co., Ltd. brochures).

Figures 2.23 and 2.24 show some similar information extracted from Tonen Corporation's literature on its Forca carbon fiber: Figure 2.23 shows some of the forms in which it is available, and Figure 2.24 gives some typical properties.



From pure, low viscosity petroleum pitch.



Cloth



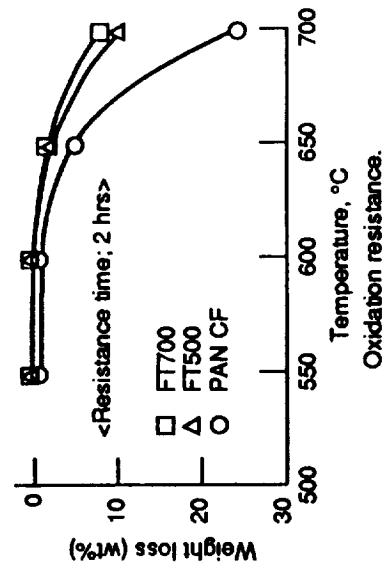
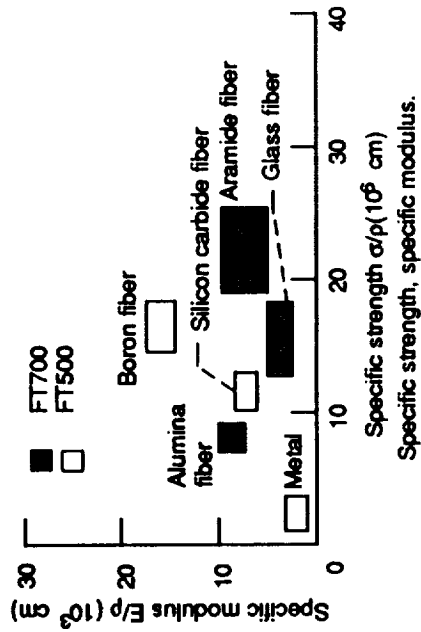
Pultruded pipe

Pultruded pipe



Prepreg

Figure 2.23. Some available forms of Forca carbon fiber (extracts from Tonen Corp. brochures).



	Properties	Units	FT700	FT500
Form of fiber	Filament diameter yield (3K base)	μ g/m	10 0.52	10 0.51
Physical properties	Density	g/cm	2.16	2.14
Mechanical properties	Tensile strength tensile modulus elongation	MPa(Ksi) GPa(Msi) %	3300(470) 700(100) 0.5	3300(430) 500(70) 0.6

FORCA typical properties, Tonen Corp.

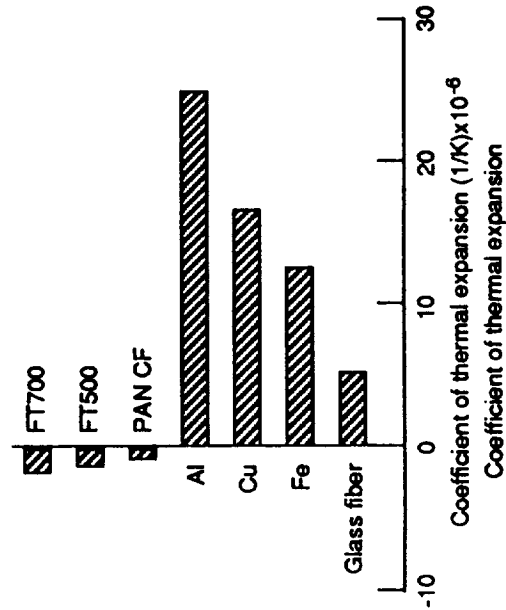


Figure 2.24. Typical properties of Forca carbon fiber (extracts from Tonen Corp. brochures).

Refractory metal fibers. A few high-temperature, high-strength refractory metal fibers are available in the United States, as shown in Table 2.7. The primary application for such fibers is in incandescent light bulbs. These fibers are ductile and strong at high temperatures but are rapidly attacked by air. Thus, they have primary potential in nonoxidizing environments--as in space applications--but if properly protected may be of use as ductile strengthening phases in other applications as well. The JTEC panel did not encounter any information that there was work underway in Japan on such fibers.

Table 2.7
Refractory Metal Fibers
Available in the U.S.

Fiber	Company
W-218CS	GE Phillips Elmet GTE
W-1ThO ₂	GE Phillips Elmet GTE
W-3Re-Ge	-----
W-Re-HfC	-----
Mo-Hf-C	GTE
Mo-Hf-C (380- μ m diam)	Metadyne Inc.

Summary Assessment of Available Fibers

Figure 2.25 is a plot of room temperature tensile strength versus modulus for a variety of the fibers presented above. Note that even at room temperature, few of the current fibers have strengths near or above 3 GPa combined with moduli above 300 GPa. However, to achieve the full potential of advanced composites, fibers are needed with such properties, not only at room temperature but at temperatures to 1600°C. Figure 2.26 is a summary of the properties of a number of classes of known fibers as a function of temperature. Even the short-time tensile properties drop off in the 1000° to 1200°C range. Thus, we can expect that long-time creep strengths will be substantially lower. This means considerable effort will be required by both the United States and Japan to improve their fibers so as to reap the benefits of low-density, high-strength composites for high-temperature aerospace applications.

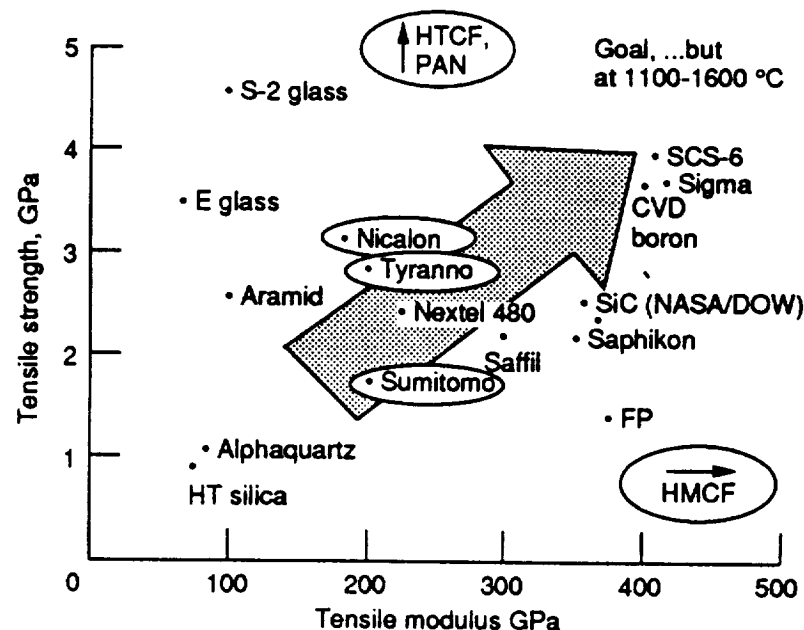


Figure 2.25. Tensile strength versus modulus for fibers at room temperature.

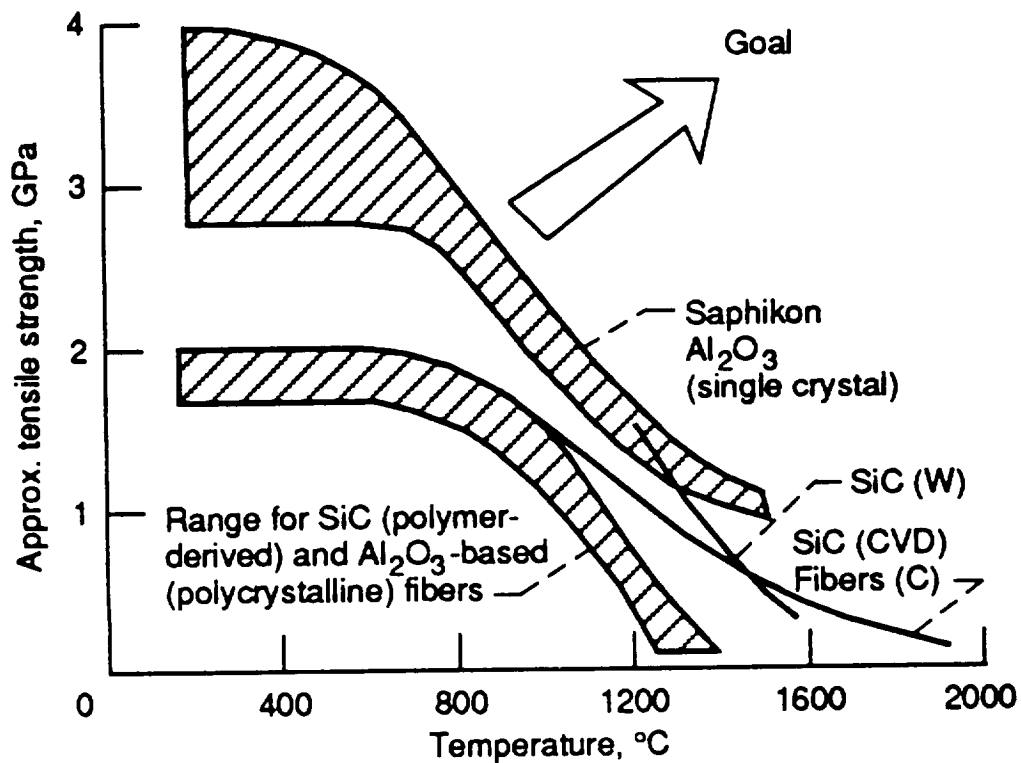


Figure 2.26. Tensile strength of fiber classes at high temperatures.

Japanese Plans for Fiber Production

As shown in Figure 2.27, an effort has been started in Japan to develop the improved production technology to convert current (and surely) future fibers to commercial structural forms, even though optimum fibers are yet to be developed. Data on the output, sales, etc. of this organization were not available.

Capital: 70M¥ at start: to increase to 2B¥

- 70% – Japan Key Technology Center
- 9% – Mitsubishi Electric Corp.
- 9% – Nippon Steel Corp.
- 6% – Toyoda Automatic Loom Works, LTD.
- 3% – Arisana MFG. Co., LTD.
- 3% – Mitsubishi Rayon Co., LTD.

R&D of 3D weaving of strong inorganic, organic, and metallic fibers and of technology for structural use.

Figure 2.27. A new corporation for composite fabrication:
3-D Composite Research Corporation, 1988.

WHISKERS AVAILABLE IN THE UNITED STATES AND JAPAN

Whiskers are generally small diameter (less than a micron), short single crystals grown by some vapor process (length to diameter is usually greater than 100:1). Table 2.8 shows some of the small number of different whiskers produced by the United States and Japan. In the past great interest existed in using whiskers to "toughen" ceramics and reinforce a range of ceramic, intermetallic, and metal matrices. In general, it has recently been recognized that such whiskers require careful handling owing to potential health issues, and thus limited interest was expressed in expanded whisker research among the Japanese companies that the JTEC panel visited.

Table 2.8.
Whiskers Available in the U.S. and Japan

(a) United States

Fiber	Company
Tokawhisker (SiC_w)	Textron (U.S. distributor for Tokai Carbon)
SiC_w (0.3- to 0.6- μm diam, 3 to 24 μm long)	Advanced Composite Materials Corp.
Silar (SiC , 1- μm diam)	Arco Metals - Silag
VLS (SiC , 4- to 7- μm diam)	Los Alamos National Laboratory

(b) Japan

Tokawhisker (SiC_w , 0.1- to 1- μm diam, 10 to 100 μm long)	Tokai Carbon
$\text{K}_2\text{Ti}_6\text{O}_{13}\text{W}$ (0.2- to 0.3- μm diam, 10 to 20 μm long, $\rho = 3.3 \text{ g/cm}^3$, TS = 6.9 GPa, E = 274 GPa)	Otsuka Chemical
α - or β - $\text{Si}_3\text{N}_4\text{W}$ (0.1- to 1.5- μm diam, 3 to 42 μm long)	Ube
SiC_w (1.5- μm diam, 1 to 100 μm long)	Toteho
Magnesca ((MgO)W, 2- to 10- μm diam, 100 to 1000 μm long)	Mitsubishi Mining and Cement
Alborex ((9Al ₂ O ₃ ·2B ₂ O ₃ ·Al ₂ O ₃)W, 0.5- to 1- μm diam, 10 to 30 μm long)	Shikoko Chemicals
(MgSO ₄ ·5MgO·8H ₂ O)W (1- μm diam, 50 μm long)	Ube

FINAL REMARKS

Figure 2.28 presents this author's personal view of one possible scenario that might be followed by the Japanese in their efforts to expand their commercial advanced composite business. Currently they have a national research effort underway on functionally graded materials (see Chapter 4 of this report). That effort could contribute to building skills in applying thin coatings to fibers by such methods as chemical vapor deposition, and in analyzing very thin fiber/matrix interfaces. Such an effort could significantly support the ongoing programs on fiber development and composite application and would couple well with Japan's evolving industrial capability to manufacture composites for mass markets. In combination, such skills and abilities indicate that in this field Japan will be positioned to be a strong competitor of the United States, whose current capability in manufacturing advanced high-temperature composites is both limited and fragmented.

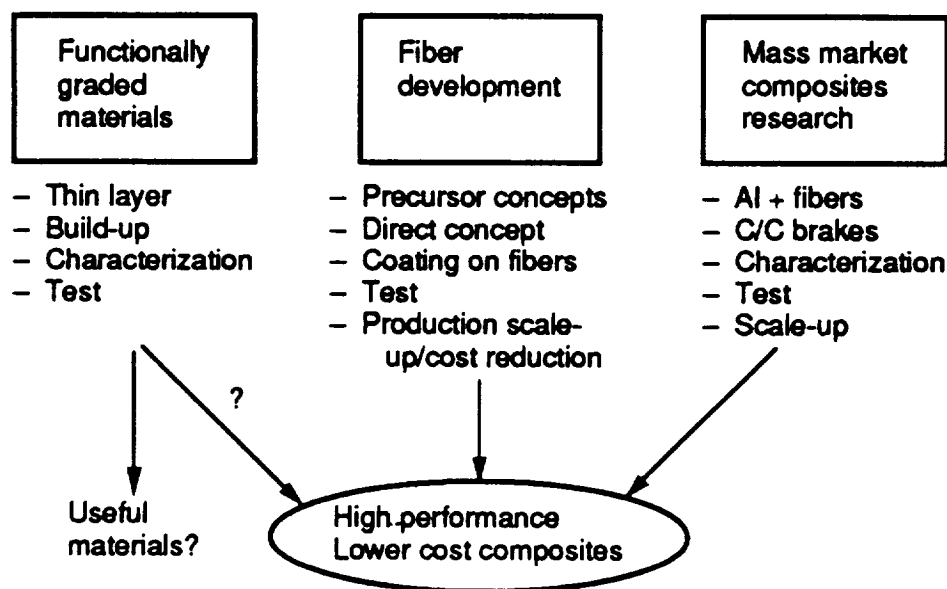


Figure 2.28. A possible scenario for commercial expansion of advanced composites capabilities.

By way of comparison with this JTEC panel's findings, Figure 2.29 summarizes the findings of the 1988 survey on inorganic composite materials in Japan by the Office of Naval Research (Ref. 2.1). One key observation is that the recent efforts by the Japanese to establish joint programs on supersonic/hypersonic propulsion systems with U.S. engine companies, coupled with the knowledge gained in the completed *Jesedai* program on engine composites, would certainly strengthen Japan's abilities to eventually produce and export commercial aircraft engines. A second observation is that Japan has recently started a national effort to conduct research on high-temperature composites for extreme environments: such composites will be the basis for the high-value-added components that must be developed to enable future aircraft engines to be commercially viable. These high performance composites will be the "computer chips" of future aerospace propulsion and power hardware.

- Japan invited U. S. engine companies to participate in (and get ¥ for) work on M3-5 transport.
- JESEDAI Program (1981-1988) completed and 1000 page handbook published.
- Tonen SiNB fiber announced and SiN being pilot-produced.
- FGM approach to fibers being pursued via CVD, etc., but still no major CVD fiber effort.
- Project for high temperature composites for use in severe environments started in 1989 (1989-1996) at ¥1B in '90.
- Decrease in whisker efforts due to health issues.

Figure 2.29. Differences observed in 1990 visit versus ONR assessment of Japan's fiber programs (9/88, pub. 11/89).

Better high-temperature fibers are the key to high-performance, lightweight composite materials. Current U.S. and Japanese fibers still have inadequate high-temperature strength, creep resistance, oxidation resistance, modulus, stability, and thermal expansion match with some of the high-temperature matrices being considered for future aerospace applications. In response to this clear deficiency, both countries have research and development activities underway. Once successful fibers are identified, their production will need to be taken from laboratory scale to pilot plant scale. In such efforts it can be anticipated that the Japanese decisions will be based on longer term criteria than those applied in the United States. Since the initial markets will be small, short-term financial criteria may adversely minimize the number and strength of U.S. aerospace materials suppliers to well into the twenty-first century. This situation can only be compounded by the Japanese interests in learning to make commercial products with existing materials so that when the required advanced fibers eventually do arrive, their manufacturing skills will be well developed.

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CHAPTER 3

CERAMIC MATRIX COMPOSITES

RESEARCH AND DEVELOPMENT IN JAPAN

William B. Hillig

INTRODUCTION

The ability to sinter and produce complex shapes of silicon carbide (SiC) and silicon nitride (Si_3N_4), acquired in the 1970s, led to the major efforts in the United States, Europe, and Japan to produce ceramic components for turbine and diesel applications--a goal that had been previously considered to be unachievable. In such uses, the components are subjected to very high stresses and temperature. The attractiveness of using ceramics instead of state-of-the-art high-temperature superalloys is that ceramics in general have (1) higher temperature capability, (2) better environmental resistance, and (3) lower density, leading to lower overall weights and decreased inertial loadings.

The disadvantage of ceramics is that their strength is notoriously sensitive to the presence of even microscopic imperfections in the materials introduced during manufacture, handling, or service. When failure occurs, it is often sudden and without warning; hence, there has been focus on ceramics that are relatively tough, i.e., relatively insensitive to flaws. Monolithic SiC is an especially strong, stiff, creep-resistant ceramic, whereas Si_3N_4 is almost as good in these regards but is considerably tougher. Even so, the toughness of monolithic Si_3N_4 is marginal for the above applications.

One approach to overcoming this deficiency is to enhance the toughness of the base ceramic by dispersing a second material throughout it to make crack propagation more difficult. If the dispersed material is in the form of whiskers (fine fibers), considerable enhancement of the toughness of the reinforced ceramic can be achieved, depending on the whiskers' size, concentration, and their coupling

to the surrounding matrix phase. This approach is being extensively pursued in Japan, especially by the introduction of fine SiC whiskers into Si_3N_4 . Such ceramic composites are called "fiber-reinforced ceramics" (FRC) in Japan.

In a second approach that is almost the inverse of the preceding one, the overall properties are generally dominated by those of strong continuous filaments coupled together by a surrounding matrix phase. Ceramic composites that are very resistant to catastrophic failure can be achieved when suitable filaments are available: the filaments must be stable in the use environment and compatible with the matrix. The approach based on continuous filament reinforcement of the ceramic matrix is being widely investigated in the U.S., France, and Germany. In these countries ceramic composites are called "ceramic matrix composites" (CMC).

The difference between the terms CMC and FRC suggests a difference in mind set regarding the expectations and intended purpose of ceramic composites, but both terms refer to high-performance reinforced ceramic composites. For clarity, the term CMC will be used throughout this chapter. Although Japan is a major supplier of both whisker and continuous reinforcement materials, much of its effort on ceramic composites is focused on the whisker reinforcement approach outlined in the next section. The major issues relative to CMCs are summarized as follows:

- Potential for overcoming deficiencies of monolithic high-performance (fine) ceramics

- Processing difficulties

- Physical compatibility between matrix and fibers

- Chemical compatibility between matrix and fibers

- Limited choice of reinforcements

- Need for fiber coating

PROGRESS AND ISSUES IN THE DEVELOPMENT OF CMCS

Interest in high-strength fiber-reinforced composites was stimulated in the 1950s by work that showed that very strong glass fibers could be made with strengths attractive for high-performance aircraft engine applications (Refs. 3.1-3.3). It was also discovered that many materials could be made in the form of extremely high-strength whiskers (Ref. 3.4). In principle, high-strength whiskers and fibers could be made to carry enormous loads when properly aligned and embedded in a suitable polymer, metal, or ceramic matrix material.

The first major demonstration that fiber reinforcement can dramatically increase the toughness of a ceramic was demonstrated in the United Kingdom in 1969 on a composite consisting of carbon fiber reinforced vitreous silica (Ref. 3.5). Similar results on various other glass (especially borosilicate) and ceramic matrices reinforced with carbon fiber were achieved in the U.K. by two independent groups during the next two years. A composite was also investigated which consisted of continuous filamental SiC embedded in a glass ceramic matrix.

Concurrently, Aveston, Cooper, and Kelly at the National Physical Laboratory in the U.K. did theoretical modeling of the mechanical properties and failure behavior of ceramic matrix composites (Ref. 3.6). This theoretical work endures as a cornerstone in the foundation for understanding the mechanical behavior of unidirectional fiber reinforced composites.

This burst of activity in the early 1970s on fiber-reinforced ceramics was followed by a hiatus due, at least in part, to the considerable promise shown by monolithic ceramics such as SiC, Si_3N_4 , and sialon, and to the optimistic view that carefully processed monolithic (i.e., unreinforced) ceramics would meet the requirements for heat engine applications. (Sialon is a high-temperature strong ceramic that results from alloying Si_3N_4 and aluminum oxide, Al_2O_3). Furthermore, suitable fiber reinforcements were not yet available; also, fabrication of fiber-reinforced ceramics is more difficult than fabrication of monolithic ceramics.

Interest in CMCs was reawakened through the availability of new high-temperature reinforcement fibers. In the United States, a process was discovered for making SiC whiskers in quantity cheaply (Ref. 3.7). These whiskers have good thermal stability but are very small in size (0.2-0.5 microns diameter, with maximum length-to-diameter ratio of about 30). In Japan, a process was invented by Yajima for spinning and then heat-stabilizing a polycarbosilane resin to form a 7-10 micron diameter, high-strength Nicalon fiber (Ref. 3.8). The heat-stabilization step is an oxidation process that cross-links the spun resin fiber to prevent it from becoming liquid in the subsequent even higher temperature process step needed to convert the resin into a ceramic fiber. The resultant fiber material approximates SiC carbide in both oxidation resistance and chemical properties. However, this fiber thermally degrades, losing strength when heated above 1100-1200°C because of the oxygen introduced in the heat-stabilizing step. These new SiC-type reinforcements expanded the potential for the two somewhat separate classes of fibrous composites, that is, continuous and discontinuous fiber reinforcements.

The range of possible ceramic composite systems was further expanded by the development of other high-temperature fibers. Table 3.1 lists the fibers that are potentially useful reinforcements. The availability of new reinforcements plus the recognition that tougher ceramics were required for high-temperature heat engine applications led to renewed activity in fiber-reinforced ceramic matrix composites.

Table 3.1
Ceramic Fiber Reinforcements

Filament Material	Diameter (Microns)	Room Temp. Strength (GPa)	Young's Modulus (GPa)	Approx.* Max.Temp. (°C)	Status/ Source
Al ₂ O ₃ (mx)	250	2.80	400	ca 1400	US
Al ₂ O ₃ (px)	20	1.40	300	1200	US
Boron	100-200	2.75	400	500-700	US
Carbon	7-10	1.4-5.5	200-700	2200	US/JA
Mullite	10	1.70	150	1100	JA
Mullite (+B ₂ O ₃)	10	1.70	150	1100	US
SiO ₂	10	1.40	70	1000	US
SiC					
-CVD	140	3.45	425	ca 1450	US
-Polymer-derived	10-15	2.40	190	1100-1300	JA
Whiskers					
-SiC	0.2-1	ca 20	480	>1600	JA
-Si ₃ N ₄	0.2-1	ca 10	275	>1600	JA

* Temperature limits depend on time and environment; (mx) = monocrystalline; (px) = polycrystalline.

A major joint research effort was undertaken by the United Technologies Research Center (UTRC) in conjunction with Corning Glass Works (CGW) (Ref. 3.9). This effort focused first on fused silica reinforced with carbon fiber and then on several lithium aluminosilicate crystallizable glass ceramics reinforced with Nicalon fiber. The UTRC-CGW work, particularly that based on glass ceramic technology, has greatly advanced the state of the art of continuous fiber reinforced ceramic composites.

As first shown by work at the Oak Ridge National Laboratory, incorporation of SiC whiskers into Al₂O₃ resulted in a fourfold increase in toughness (Ref. 3.10). This material has been subsequently refined to achieve superior ceramic cutting tools.

The use of whisker reinforcements for continuous filament reinforcement presents certain difficulties, including their purported carcinogenicity. The whiskers must be essentially handled as powders. Because of their rod-like shapes, the achievable packing density of such randomly oriented whiskers is low, which in turn reduces the degree of toughening. Packing can be improved by aligning the fibers, but such ordering is difficult. Comminution of the whiskers also allows the concentration of the reinforcement to be increased, as has been demonstrated in the Si₃N₄/SiC system (Ref. 3.11).

Incorporation of whiskers or continuous fibers into the body of a ceramic interferes with attainment of a fully dense structure by conventional pressureless sintering. Accordingly, the use of fiber reinforcements has increasingly focused attention on such alternative techniques as hot-pressing and hot isostatic pressing (HIP), chemical vapor infiltration (CVI), and liquid-state methods involving molten glass-ceramics, sol-gel or polymeric ceramic precursor resins, and melt infiltration. The use of particulates to reinforce the matrix is an alternative that allows conventional pressureless sintering to be used; however, particulate reinforcement offers less potential for toughening.

Japan has made substantial contributions to the international reinvigoration of the ceramic composites field by making commercially available in substantial quantity continuous Nicalon (TM) silicocarbon filaments (by Nippon Carbon Company) and the related Tyranno (TM) titanosilicocarbon filaments (by Ube Industries). In addition, SiC and Si₃N₄ whiskers have also been made commercially available in quantity. For approximately a decade, Japanese companies have been the major suppliers of these core materials. These capabilities plus Japan's commitment and strength in the area of fine high-performance ceramics provide a powerful base for technological leadership in the area of high-temperature ceramic composites. How this is being addressed is presented in the remainder of this chapter. The evolution of CMCs is outlined in Table 3.2.

JAPAN'S NATIONAL PRIORITIES AND GOALS

Japan's interest in ceramic composites is part of a larger interest in high-temperature, high-performance structural materials for power generation, transportation, and aerospace applications. The substantial technical resources in Japan are being focused to a large degree by the government through its various ministries and agencies. This is achieved directly through the work at the various governmental institutions and through influencing the various industries via funding, and indirectly through a cultural predilection to cooperation with government.

The Ministry of International Trade and Industry (MITI) selects and plans areas of strategic importance to the nation's future economic well-being. Areas of high priority include energy conservation (Moonlight Project) and the development of supersonic and hypersonic vehicles which in turn are intended to support the emerging subsonic air transport industries. There is a national strategy for Japan to become a major participant, if not a world leader, in air transport and aerospace technologies. In addition to various government organizations outside of MITI, such as the National Aerospace Laboratory (NAL), the national universities and industry are also participating in various aerospace-oriented efforts.

Table 3.2
Key Events in CMC Evolution

Year	Event	People	Country
1969	Glass/C fiber composite made; tough; wood-like failure	Crivelli-Visconti & Cooper	U.K.
1971	Theoretical base presented	Aveson, Cooper & Kelly	U.K.
1975	SiC whisker process invented	Lee & Cutler	U.S.
1976	Continuous Si-C-O (Nicalon) fibers	Yajima	Japan
ca 1980	LAS/Nicalon technology developed	Prewo et al.	U.S.
1986	Al ₂ O ₃ /SiC (wh) shows toughness	Wei & Becher	U.S.
1986	Theory refined	Budiansky, Evans & Hutchins	U.S.
1986	CVI process demonstrated	Naslain	France
1986+	Many advances in processing, systems, theory		U.S.
1986+	Reinforcement availability		U.S. & Japan

The success of both the ceramic gas turbine portion of the Moonlight program and the aerospace strategy are dependent on the future availability of much improved high-temperature, high-performance structural materials, including ceramic matrix composites. Materials development work needed for the high-efficiency ceramic gas turbine effort is included in the scope of the Moonlight program, which was initiated in 1988. The performance goals are 42% efficiency in the conversion of the energy content of the fuel into electricity, an inlet gas temperature of 1350°C (the higher the temperature the greater the efficiency), and a power output of 300 KW. As shown in Figure 3.1, ceramics and FRCs were identified as candidate materials for the hottest working parts of the turbine because they offer higher temperature capability than state-of-the-art superalloys. Furthermore, ceramics are comprised of readily available materials.

なぜ、セラミックガスタービンなのか？

Why a Ceramic Gas Turbine (CGT)?

セラミックガスタービンとする理由

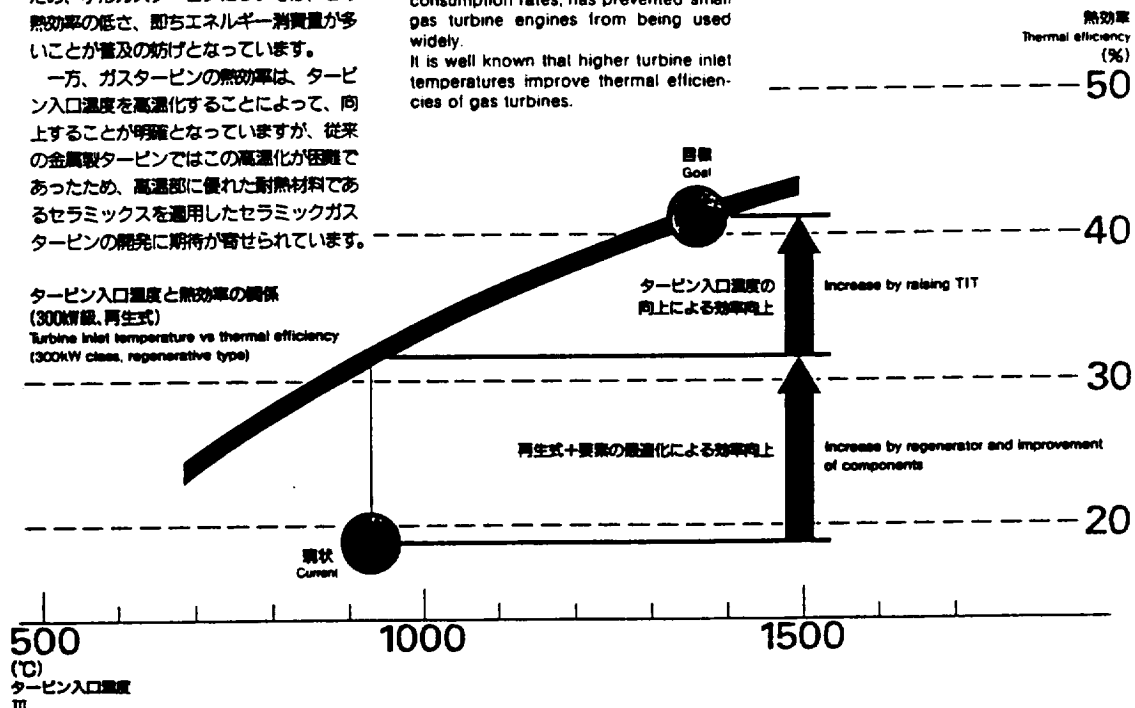
ガスタービンの唯一の欠点は、その熱効率の低さにあり、現在20~30%に止まっています。特に、ガスタービンの熱効率は出力が小さくなるにつれて急速に低下し、500kW以下の小形級では15~20%程度となるため、小形ガスタービンについては、この熱効率の低さ、即ちエネルギー消費量が多いことが普及の妨げとなっています。

一方、ガスタービンの熱効率は、タービン入口温度を高温化することによって、向上することが明確となっていますが、従来の金属製タービンではこの高温化が困難であったため、高温部に優れた耐熱材料であるセラミックスを適用したセラミックガスタービンの開発に期待が寄せられています。

A Ceramic Gas Turbine (CGT, a gas turbine with major components made of ceramics) has such advantages as: The only, yet vitally-important, shortcoming of gas turbine engines is its poor thermal efficiency, which is as low as 20 to 30%. Thermal efficiency decreases sharply as an engine's output decreases, and it is as low as 15 to 20% for small engines under 500kW. Such low thermal efficiency, meaning high fuel consumption rates, has prevented small gas turbine engines from being used widely.

It is well known that higher turbine inlet temperatures improve thermal efficiencies of gas turbines.

However, conventional metallic turbine components are unable to tolerate the higher turbine inlet temperatures that could remarkably increase the thermal efficiency. Now industries are looking forward to the realization of Ceramic Gas Turbine engines that use highly heat resistant ceramic materials for the turbine components exposed to high temperatures.



考えられるセラミック材料

Candidate for Ceramic Materials

Si₃N₄・Sialon	高温強度・靱性が高く耐熱衝撃性、耐摩耗性が良好	High temperature strength, toughness, thermal shock resistance, wear resistance
SiC	高温強度が優秀で、熱伝導、耐摩耗性、耐食性も良好	High temperature strength, thermal conductivity, wear and corrosion resistance
FRC	Si ₃ N ₄ ・SiC等の繊維強化をしたもので高靱性・高強度	Fiber-reinforced Si ₃ N ₄ , SiC, etc. High toughness and strength
ZrO₂	高温耐食性、断熱性に優れ、コーティング材に適する	Coatings for corrosion resistance and thermal insulation, high toughness
MAS・AS	熱膨張係数が極めて少なく、耐熱変形、耐熱衝撃性に優れる	Low thermal expansion, high thermal shock resistance

Figure 3.1.

The materials performance goals to achieve the above performance are a 1500°C temperature capability, a strength of 400 MPa (60 Ksi) at 1500°C, a Weibull modulus of 20, and a fracture toughness of 15 MPa m^{1/2}. (The Weibull modulus and fracture toughness values, respectively, specify uniformity of strength and toughnesses comparable to those for structural alloys.) These are very demanding goals. The candidate materials selected for evaluation include fiber reinforced SiC and Si₃N₄ as well as several monolithic ceramics.

The corresponding work for the even more demanding supersonic\hypersonic (SST\HST) aerospace applications is titled "High-Performance Materials for Severe Environments." This is just starting as a Basic Technologies for Future Industries Project of the Agency of Industrial Science and Technology (AIST).

Temperatures as high as 2000°C are envisioned for some of the components. Interestingly, CMCs are not included in the list of candidate materials, which includes carbon-carbon composites for the highest temperature requirements. Intermetallic compounds or composites based on molybdenum or niobium have been identified for use in the range 1100°C to 1800°C--and composites based on titanium aluminide at lower temperatures. Other than carbon fibers, no continuous filaments are available that maintain strength and are creep-resistant above about 1300°C. Even so, the present long-term plans do not include work to develop new higher temperature fibers.

The NAL organization, which is designing a hypersonic plane, is well equipped and staffed to characterize materials received from external sources for evaluation as candidate materials. However, the NAL effort does not include the development of advanced materials, even though such materials may be needed for the successful implementation of the design.

Recognition of the high temperatures that will be generated in the engines and at the leading portions of the airfoil surfaces of the envisioned high-velocity aircraft has identified a need for functionally gradient materials (FGMs). FGMs are composite materials which continuously grade from a metal on the one side to a ceramic on the other, through the thickness of the structure. The role of the ceramic layer is to endure the high temperature and to reduce the heat flow through the thickness so that the metal portion will remain cool enough to retain adequate strength and rigidity. FGMs are being developed at the national laboratories operated by AIST, at the national universities, and in industry. The Panel visited some but not all of these laboratories. Some additional information on the FGMs in Japan is covered in Chapter 4.

MAJOR TECHNICAL THRUSTS AT GOVERNMENT AND UNIVERSITY FACILITIES

Through MITI's planning and funding procedures, there is considerable overlap in the technical areas pursued at the various Government Industrial Research Institutes (GIRIs) which are operated by AIST. MITI/AIST also fund programs in industry that support the planned goals; thus, there is close coupling between CMC work performed in industry and in the GIRIs. Although the national universities are independently funded, there is considerable correlation between the work at the universities and that at the GIRIs because many of the faculty serve on review and oversight committees for AIST. Industry and the universities can work together directly.

For these reasons, the research efforts relating to CMCs in Japan will be treated according to the various major technical areas rather than according to organization. These themes are (1) silicon carbide (SiC) and silicon nitride (Si_3N_4) composites; (2) other SiC and Si_3N_4 whisker reinforced CMCs; (3) carbon fiber reinforced CMCs; (4) Hot Isostatic Pressing (HIP) and self-propagating high-temperature synthesis (SHS) processes; and (5) functionally gradient materials (FGMs). The work at one of the companies visited will be discussed separately because it did not lend itself to the preceding categorization.

Due to the JTEC panel's overall time considerations and the briefness of the visits to the laboratories and organizations, the comments that follow are "snapshots" rather than comprehensive pictures of the Japanese efforts in the various areas. On the other hand, the sites visited were major centers for CMC research.

Silicon Carbide and Silicon Nitride Composites

Evaluations relating to the Gas Turbine Program of the Moonlight Project have identified monolithic SiC and Si_3N_4 as major candidate materials for use as high-temperature components. Thus, it would be desirable to render these materials more damage tolerant; for example, by introducing whiskers into them. Among the issues are (a) what is responsible for the toughness of the monolithic structural ceramic materials, (b) how best to incorporate the whiskers, and (c) what benefit is derived.

The factors affecting the toughness of Si_3N_4 is the subject of a basic study at Osaka University under Assistant Professor Tanaka, in which monolithic material is made from very pure starting material and then additives are systematically introduced to determine their effects on strength and toughness (Ref. 3.12).

Pressureless sintering and hot pressing of SiC whisker reinforced Si_3N_4 is being investigated at Osaka-GIRI under the direction of Mr. Tamari (Ref. 3.13). The former technique, even at an extremely high temperature (2000°C), required large

proportions of sintering aid ($Y_2O_3 + La_2O_3$) to achieve full density--20% and 30% when the SiC whisker content was 10% and 20%, respectively. By hot pressing, the temperature could be dropped to 1800°C. Good strength and a modest improvement in toughness was achieved.

A rather different approach is under study by Dr. Wakai at Nagoya-GIRI in which an amorphous Si-C-N powder prepared from a polymeric precursor plus 8% of sintering aid was shown to lead to full densification at 1650°C (Ref. 3.14). At 1600°C, this material exhibited superplastic behavior, i.e., high ductility with 150% elongation. This behavior suggests the possibility of incorporating fibers and shaping by forge-like processing. The strength and toughness of this SiC-Si₃N₄ composite was typical of that for monolithic Si₃N₄.

Another effort at Nagoya-GIRI under Dr. Ohji includes setting up a sophisticated test facility for determining the basic mechanical properties of structural ceramics and CMCs such as Si₃N₄ and SiC whisker reinforced Si₃N₄ (Ref. 3.15). This facility includes testing at elevated temperature of tensile strength and modulus, fracture toughness, static and cyclic fatigue, and strain rate effects. This effort also includes detailed microscopic investigation of defects and crack tip processes. In short, this facility offers state-of-the-art capability and expertise.

Other Whisker Reinforced CMCs

Because of the availability of SiC and Si₃N₄ whiskers, the use of these materials to reinforce matrices other than those discussed above has also been investigated. As an extension at Osaka-GIRI of the above work on the reinforcement of Si₃N₄ by SiC whiskers, analogous studies were made in which the matrix was tetragonal zirconia polycrystals (TZP), a ceramic oxide rendered tough by a special phase transformation mechanism. The results were not encouraging: although material containing up to 30% whiskers could be made nearly fully dense by hot pressing at 1500°C, the addition of whiskers doubled the toughness at the price of halving the strength. In a similar study in which 20% of Si₃N₄ whiskers were used to reinforce alumina, the toughness increased 50% over the unreinforced matrix, and the strength decreased 25%. It was necessary to limit the hot pressing temperature to 1700°C to prevent a chemical reaction between the whiskers and the matrix.

At Nagoya-GIRI, Dr. Kamiya and colleagues have studied the addition of SiC whiskers to TiC, TiB₂, and to NbC (Ref. 3.16). Increasing the whisker content did not seriously inhibit achieving nearly complete densification. Hot pressing at 1850 and 1900°C was required for TiC and TiB, but 1600°C was sufficient with NbC containing 1% of Cr₇C₃ as a sintering aid. About a 20% increase in strength and toughness resulted in the cases of TiC and TiB for whisker contents up to 30%. A similar addition resulted in an almost doubling of strength and a 20% increase in toughness when NbC was the matrix.

Carbon Fiber Reinforced CMCs

Considering that C fibers are the only commercial continuous fibers that maintain high strength to the temperatures specified in the Gas Turbine goal, it was surprising that so little effort has been devoted to studying the use of C fibers in CMCs. However, the use of C fibers is complicated by the vulnerability of C to oxidation at high temperature, by the reactivity of C with many matrix materials, and by the marked directionality of thermal expansivity, i.e., by very low thermal expansivity along the fiber length but high expansivity in its cross-sectional direction. The use of pitch- and of polyacrylonitrile (PAN)-derived C fibers to reinforce mullite was investigated at Nagoya-GIRI (Ref. 3.17). (Mullite is a high-temperature oxide having low thermal expansivity. It is important in CMCs to match the expansivities of the matrix to that of the fibers.) The composites were produced by hot pressing at 1600 or 1700°C. The choice of Si or Si+N containing resin binders was found to affect the strength and toughness in complex ways. In particular, the combination of a 1700°C processing temperature with PAN-derived C fibers and Si+N containing a binder was found to have a disastrous effect on the strength and toughness of the composite when tested in air at elevated temperatures. Other combinations were found to exhibit strengths and very high toughness values both at room temperature and at 1200°C when tested in air. Optimization of ultimate strength rather than the fracture stress of the matrix appears to be the primary objective.

Hot Isostatic Pressing and Self-Propagating High-Temperature Synthesis

Japan is a leader in HIP equipment manufacture. Such apparatus allows processing at very high gas pressures (1000 atmospheres or more) and very high temperatures (up to about 2000°C). An otherwise porous material can usually be densified by cladding it or by some other means producing an impervious skin and then processing the material at high pressure and temperature in the HIP apparatus, causing the voids within the material to collapse. Making such equipment requires expertise in the fabrication of massive high-strength steel and the design of sophisticated, reliable controls. Therefore, it is not unexpected that HIP should be a prominent process capability in Japan.

Self-propagating high-temperature synthesis (SHS) is a long-known technique for achieving high temperatures by means of a chemical reaction. A prominent example is the Thermit process in which a mixture of powdered aluminum and iron oxide are ignited and react to form iron and aluminum oxide. This reaction leads to a temperature increase in excess of 2000°C and has been used to weld and repair steel railroad rails. Other material combinations such as titanium and carbon can also react, not only producing a high temperature but also a new material (in this example, TiC).

In an innovative program at Osaka University, Prof. Miyamoto has been combining HIP and HSH techniques to achieve new system, shape, and compositional control capabilities (Ref. 3.18). The approach is under further development at Kawasaki Heavy Industries. One of the basic concepts is to press or otherwise shape a well-blended mixture of the powdered reactants to produce a porous specimen. The specimen is coated with boron nitride (BN) serving as a parting agent, and it is placed and sealed under vacuum in a Pyrex borosilicate glass envelope, which then is also coated with BN. The envelope is then embedded in a porous self-combusting mixture of C and Ti powder, and this entire combination is placed in an HIP chamber (Figs. 3.2[a] and 3.2[b]). The temperature of the HIP unit is raised sufficiently to soften the glass, then gas pressure is applied, causing the soft impervious glass envelope to collapse against the specimen. The C+Ti mixture is then ignited by a small embedded electric resistance heater. The liberated heat in turn ignites the reactant mixture comprising the specimen. The gas pressure plus the temperature generated in the specimen cause it to densify.

The advantages of this approach are (1) the process is much faster and more energy efficient than if the entire HIP chamber had to be raised to the required temperature; (2) ordinary glass can be used as the encapsulant because it only experiences the high temperature briefly; (3) the use of glass allows the shape of the specimen having even complex geometries to be largely preserved. The temperature within the specimen can be controlled by adjusting the composition to include prereacted powder which serves as thermal ballast.

Choice of the specimen constituents determines the composition of the final product. By blending nickel, Si, and C powders, a Ni/TiC cermet composite material results. If boron is substituted for the carbon, a Ni/TiB₂ composite results. Other materials that have been made include TiC/TiB₂, TiC/alumina, and MoSi₂/TiAl composites. By grading the proportions of the constituent powders, it is possible to grade the resultant composite in the representative case of the Ni-TiC system from a 30%Ni/70%TiC to a 100% TiC composition, over which range the structure changes from Ni being the continuous phase that bonds the TiC, to the inverse in which TiC is the continuous phase with Ni present as inclusions. The case in which Ni is continuous exhibits a five-fold greater toughness than the reverse case. By adjusting the proportions of TiC powder to that of 1:1 Ti+C powders, the maximum temperature and microstructure of the TiC can be controlled. The use of nitrogen as the pressurizing gas provides yet another process option, because under HIP operating conditions, nitrogen can be reactive so that nitrides and surface nitriding, for example of niobium, is possible. These studies indicate the strength and potential of mating the HIP and SHS processes. At Kawasaki Heavy Industries, a graded composite of MoSi₂-TiAl has been produced in this way. The MoSi₂ results from the reaction between Si and Mo, and the TiAl results from the reaction between Ti and Al.

The ability to produce materials with properties that grade through their thickness is significant for the functionally gradient materials discussed below. The SHS/HIP approach pioneered by Prof. Miyamoto has led to a modified technique at Tohoku-GIRI, where the making of compositionally graded composites of copper-titanium

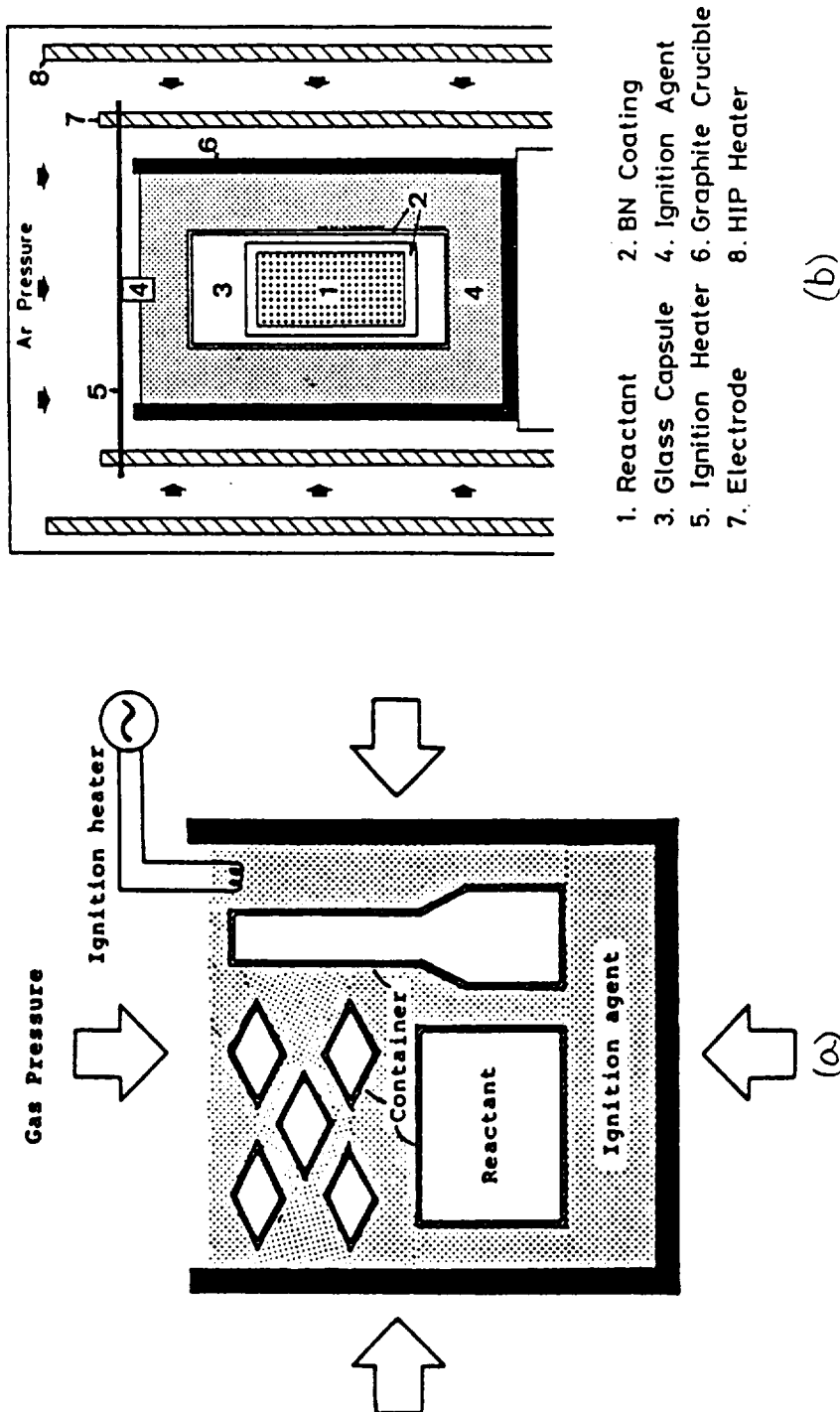


Figure 3.2. A schematic of equipment for gas-pressure combustion sintering.

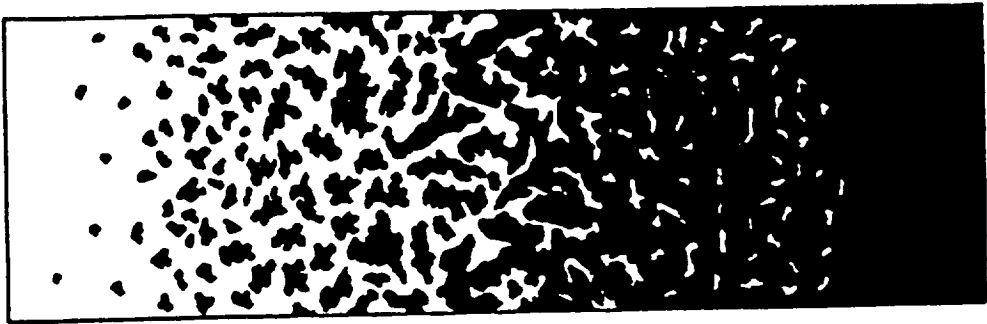
diboride has been investigated (Ref. 3.19). The forming of the graded porous starting structure is analogous to that of the above Ni-TiC system, except that the powders in this case consist of Cu, B, Ti, and TiB_2 . The particular objectives in this work are to densify the system in the face of the contraction resulting from the reaction between Ti and B, and to try to evolve a process that lends itself to the making of thin sheet-like final structures. The SHS process is performed under high-pressure water maintained at constant pressure by means of a compressed gas buffer chamber. Because of the short duration of the thermal pulse, silicone rubber proved adequate as the impervious pressure-transmitting envelope. No indication was given as to the generality of this approach.

Functionally Gradient Materials

Functionally gradient materials (FGMs) are composites in which the proportions of the constituent phases are varied in an article of interest made from the composite in order to tailor the properties locally to improve the performance of the article. In particular, the specific interest relates to the needs of the several HST/SST aerospace plane projects. Surface temperatures as high as 2000°C and temperature gradients on the order of hundreds of degrees per millimeter are envisioned. The temperature requirement exceeds the capability of known feasible metals; thus, a ceramic will be required for the high-temperature skin. On the other hand, the thermal conductivity and brittleness of the ceramics is unfavorable for good thermal shock resistance; hence, a composite system which grades from a ceramic at one surface to a continuous metallic phase at the other surface appears to offer a solution to the material requirements.

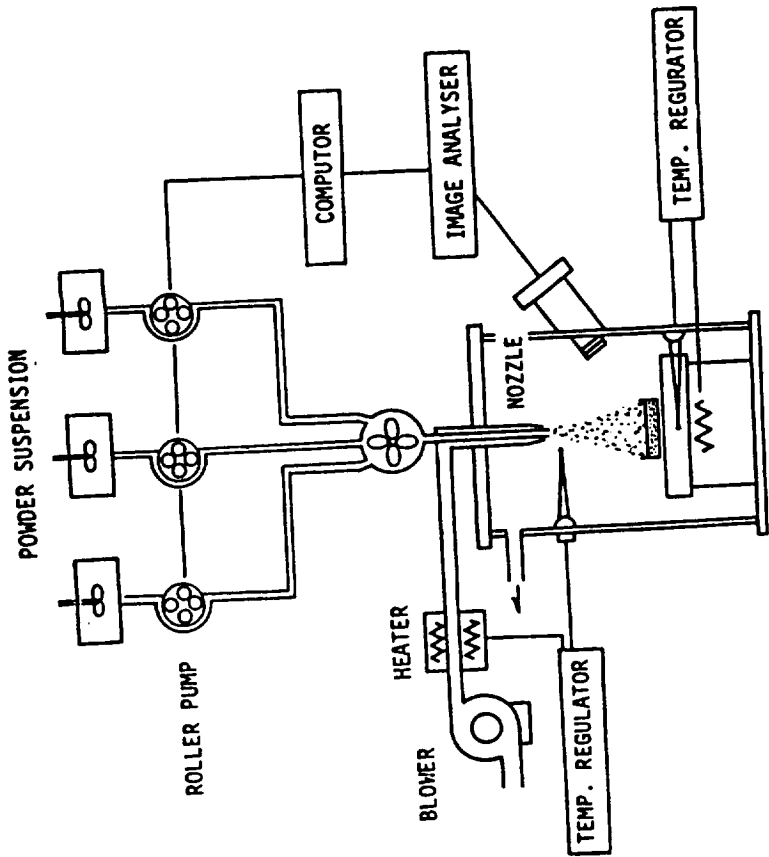
Four approaches have been identified for producing such FGMs. These are: (1) SHS, (2) powder metallurgical processing, (3) vapor deposition, and (4) plasma spraying. The first approach was discussed in the preceding section. The second approach is being pursued at Tohoku University (Sendai) and at Daiken Industries. The third strategy is also being investigated independently in another part of Tohoku University. These latter two methods are discussed below. The remaining approach will be presented as part of Chapter 4 on metal matrix composites.

Powder Metallurgical Approach. The fundamental aspects of the powder processing techniques are being investigated by Professor Watanabe, a recognized expert in the field (Ref. 3.20). Actually, this approach spans both ceramic and metallurgical technologies. Metal powders are blended with ceramic powders and dispersed in a suitable liquid vehicle. Successive layers of the slurries with increasing concentration of the ceramic constituent are sprayed onto a metallic base. The composition of the metal powder corresponds to that of the base metal or alloy. After a sufficient number of sprayed layers, the composition of the slurry corresponds to 100% ceramic. The sophisticated control of this process and the grading that can be achieved are shown schematically in Figures 3.3(a) and 3.3(b).



Schematic drawing of microstructural transition with compositional variation in powder metallurgical FGM.

(b)



Powder spray stacking apparatus.

(a)

Figure 3.3. Powder metallurgical processing for functionally gradient materials.

Complications are typically encountered when sintering these layered composite structures. The shrinkages of the various layers and the temperature ranges over which sensible sintering occurs are functions of the composition and particle size distribution of the layer. The kinds of problems that occur are indicated in Figure 3.4. These problems were largely mitigated by tailoring the particle size distributions of the layers to yield closely identical amounts of sintering. A "first approximation" adjustment in the sintering temperature was achieved by imposing a temperature gradient on the structure during the sintering process.

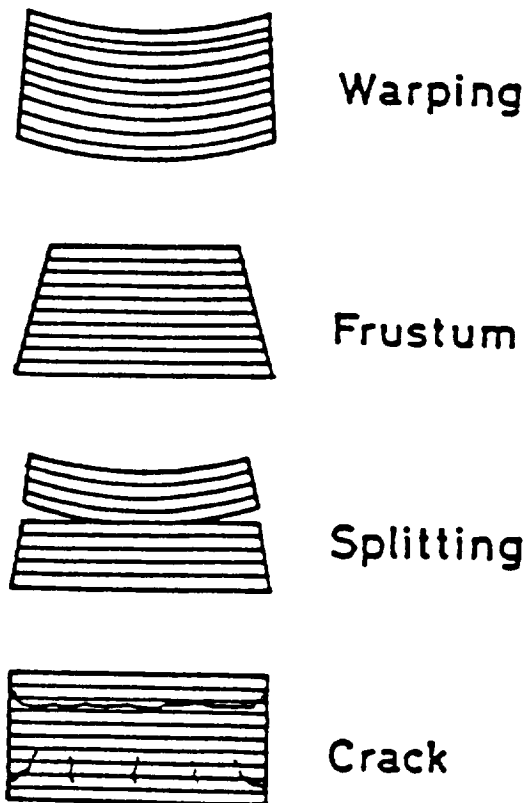


Figure 3.4. Typical sintering faults due to sintering unbalance with composition.

In order to design a satisfactory FGM, it is necessary to have a predictive model or measurements of the mechanical strength, elastic, and thermal properties as a function of the composition of the layers. The materials work at Tohoku University is augmented by that of another group that is devoted to measuring the properties of small, thin composite specimens. These are very difficult measurements, and a special apparatus and novel technique has been developed for this purpose.

To guide specifications for thicknesses, compositions, and powder characteristics, a computer program that incorporates elements of design and materials knowledge bases has been developed by Daikin Industries. There appears to be infrequent dialogue between the modelers/analysts at Daikin and the experimentalists at the university, in part because they are geographically remote from one another.

Various materials systems have been investigated to date. At Tohoku University these include stainless steel(SS)-ZrO₂, SS-Si₃N₄, molybdenum(Mo)-ZrO₂, and Mo-Si₃N₄. The system nickel-ZrO₂ was mentioned at NAL without specific credit as to where the work was performed.

The powder approach appears to be relatively straightforward, and offers a wide choice of primary constituents, as well as good microstructural control. Depending on the shape of the articles of interest, it may be possible to further enhance the quality of the composite by means of pressure-assisted sintering.

Chemical Vapor Deposition (CVD) of FGM Structures. By gradual modification of the mix of the vapor species from which the separate constituents of an FGM can be deposited, it is possible to produce a gradual shift in the composition of the deposit. The microstructure of CVD-produced materials is often quite different from that produced by the powder metallurgical method. It is not unusual for a CVD deposit to have crystal orientations or shapes that are different in the deposition direction from those in the direction parallel to the deposition surface.

In order for the CVD approach to be applicable to FGMs, the separate constituents must deposit under similar sets of conditions, e.g., temperature, pressure, and composition of the reacting gas. These conditions also depend on the choice of the starting materials. Once conditions for the codeposition of two separate materials are established, not only FGMs but also nanocomposites can be prepared. The latter materials are ultrafine particulate composites of uniform average composition. Such composites often exhibit enhanced toughness and other interesting properties (see also the section above on SiC and Si₃N₄ composites). Both the FGM and nanocomposite potential of CVD processing are being studied at the Institute for Materials Research at Tohoku University.

An FGM system that has received considerable attention is C-SiC (Ref. 3.22). In this case the purpose of the SiC outer layer is to provide protection against

oxidation of a carbon structure. Such a coating could allow carbon to be used as a combustor or other similar applications in which it is exposed to an aggressive environment. Codeposition results when a mixture of SiCl_4 and C_3H_8 (propane) are reacted with H_2 at 1 atmosphere total gas pressure at 1500°C . The gradual transition from carbon to SiC deposition is achieved by the gradual shift of the $\text{C}_3\text{H}_8:\text{SiCl}_4$ ratio from infinity to zero. Interestingly, the morphology of the carbon changes markedly with Si content. Pure C_3H_8 plus H_2 leads to a smooth carbon coating that adheres to the bulk carbon substrate. As the Si content increases, the carbon layers become more flake-like, with the flat layers perpendicular to the growth direction. As a result, considerable porosity develops in the region between the pure carbon and the pure SiC layers. The effect of this microstructure on the probable diminished transverse strength of the coating and on the oxidation resistance was not discussed. However, the enhanced compliance attributable to the porosity was judged to be advantageous with respect to improving the resistance to failure due to thermal stresses.

Daikin is also cooperating with this approach to FCMs. The computer program used in the powder approach was also used to design the optimum grading for the C-SiC system. As before, information is required relating thermal expansivity, elastic properties, and fracture strength to composition and temperature.

MAJOR THRUSTS IN CMCS IN INDUSTRY

The foci in industry CMC initiatives differ from the government and university initiatives primarily because of the need for economic success. For example, because many Japanese companies are international suppliers to U.S. and European aerospace efforts, their priorities reflect the needs and interests of their international customers as well as those of Japan. Ube Industries (UBE) was visited by the JTEC panel and serves as a case in point.

As a chemical engineering company, UBE has made a strategic decision to become a materials and components supplier to the emerging areas of electronic materials and high-technology ceramics. UBE is a source of high-purity Si_3N_4 to such ceramic manufacturers as Kyocera; UBE also produces Tyranno Si-Ti-O-C high-temperature reinforcement fibers which are important candidates for use in MMCs (metal matrix composites) and CMCs. These fibers compete with Nicalon Si-O-C fibers made by Nippon Carbon. UBE's involvement in these products has led to high technical strength in the area of inorganic silicon chemistry synthesis. This background has led to such advances as the making of high-quality Si_3N_4 whiskers, sialon ceramics, and a high-temperature all-SiC CMC that appears to exceed the goals set forth by the Gas Turbine program of the Moonlight Project.

The discovery of a process for making crystallographically and morphologically perfect Si_3N_4 whiskers has inspired UBE to seek ways of utilizing this material for composite reinforcements on a commercial scale. There is concern that their small size (0.1-1.5 microns diameter, aspect ratio about 30) and stiffness cause the whiskers to be carcinogenic. To counter this, UBE has developed a technique for producing whiskers in the form of a shaped porous block that can be infiltrated with an alloy such as 6061 aluminum. It hopes to develop a market for these.

The same amorphous Si_3N_4 starting material for making the whiskers can also be used to make sialon (Si-Al-O-N) ceramic (Fig. 3.5). By control of the processing conditions, it was found possible to make a composite consisting of controlled proportions of two crystal modifications of sialon. The alpha form consists of fine, roughly spherical grains, whereas the beta form consists of elongated grains. Elongated grains are desirable because they can act somewhat like fibers in resisting the opening and propagation of cracks, thereby conferring toughness on the material. This composite in which the constituents have identical compositions avoids the problem of chemical reaction between the constituent phases that often plagues high-temperature composites. This all-sialon composite could be made nearly fully dense by *pressureless sintering*. This material exhibited much higher strength and toughness than conventional monolithic sialon. The properties are comparable to *hot-pressed*, high-quality monolithic Si_3N_4 .

A completely different and particularly interesting homocomposite resulted from the hot pressing of a parallel array of Ti-Si-O-C fibers with or without powder, having the same composition as the fibers to 1800-1900°C (Ref. 3.23). Under these conditions, the fibers remained coherent but nevertheless deformed from a circular to a hexagonal cross-section, thereby completely filling space. The chemical composition was modified by the elimination of oxygen and by the migration of Ti in carbide form to the interface between the vestigial fibers. The resultant structure was fully dense and exhibited fiber-reinforced CMC behavior. Strength up to 1400°C (the limit of the test apparatus) was temperature independent and was representative of good quality monolithic SiC. The fracture behavior showed load-carrying capability beyond the ultimate strength maximum (Fig. 3.6). This indication of toughness was even more pronounced at 1400°C in air than at room temperature. Nominally at least, these values suggest that this material will satisfy the gas turbine requirements, and should also be of interest to the SST/HST programs. This material and its processing are in early stages of development.

There was considerable group *esprit* evident in the industrial laboratories visited; in the government and university laboratories, the dynamism varied widely from individual to individual. The industry staffs on the whole appeared to be relatively younger and more junior in terms of academic degrees, but were alert, intelligent men (none of the scientists/engineers were women). They frequently asked about the market potential and business opportunities offered by the various projects.

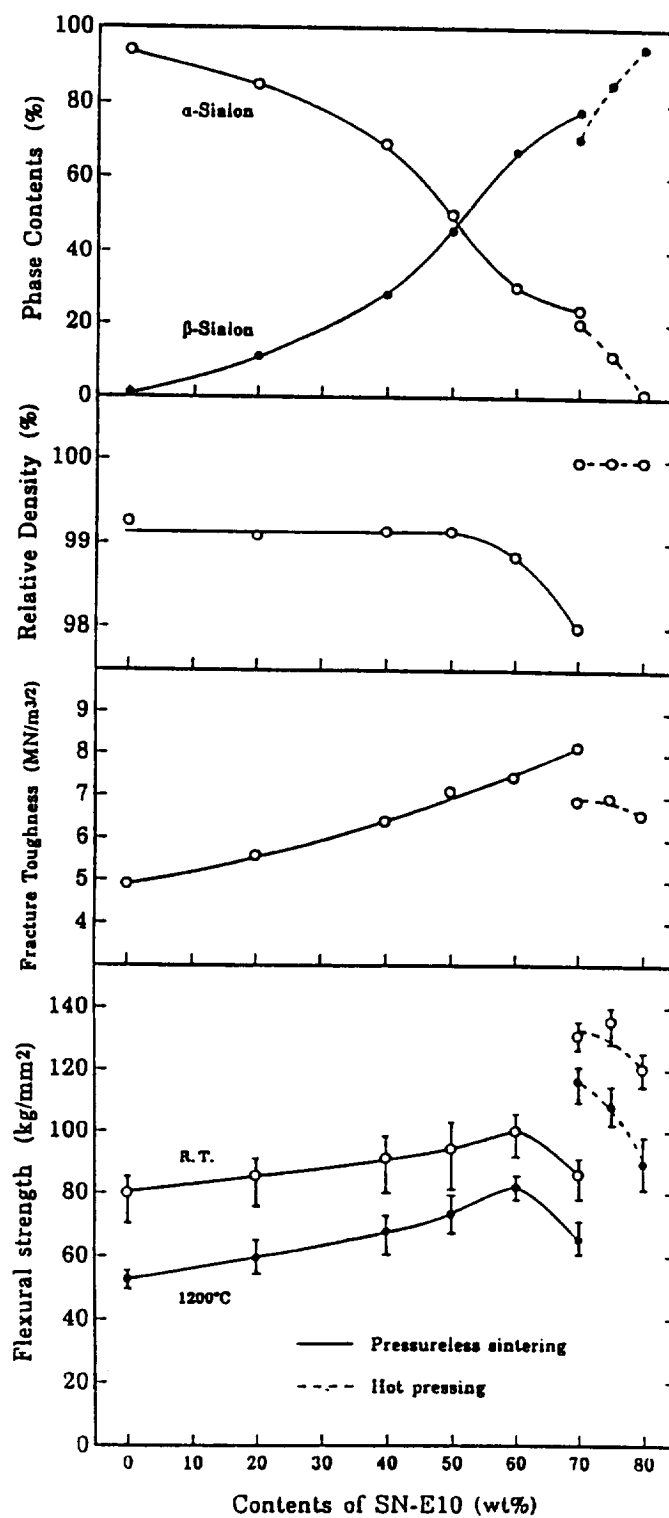


Figure 3.8. Sialon homocomposite.

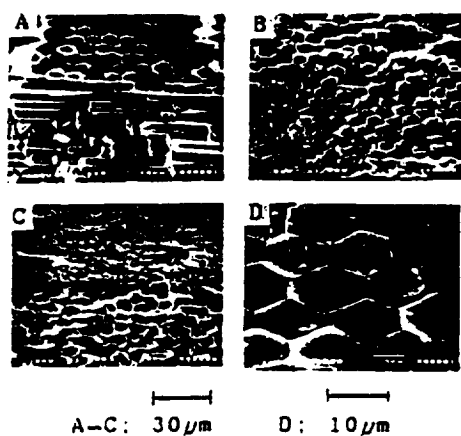


Fig. 4 Fracture surface of CMC using Si-Ti-C-O fiber.
A: plane web
B: UD sheet
C: UD sheet + powder
D: hexagonal columnar structure of fibers

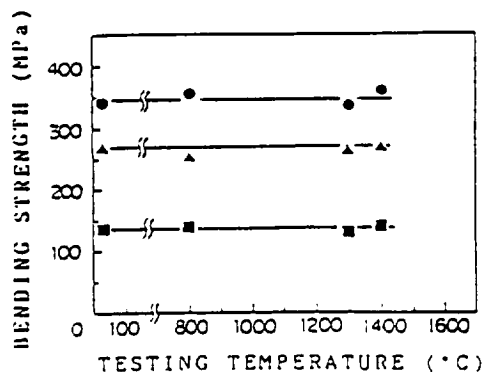


Fig. 5 Heat-resistibility of CMC using Si-Ti-C-O fiber in air
▲: UD sheet
■: plane web
●: UD sheet + powder

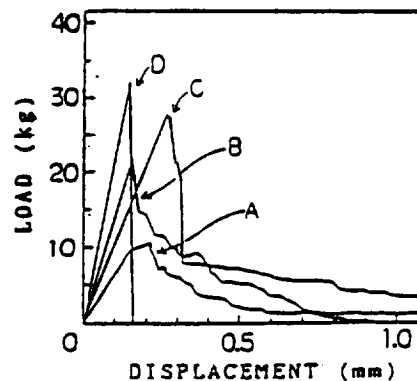


Fig. 6 Load-displacement curve for CMC using Si-Ti-C-O fiber at 25°C in air.
A: plane web
B: UD sheet
C: UD sheet + powder
D: Si-Ti-C-O powder

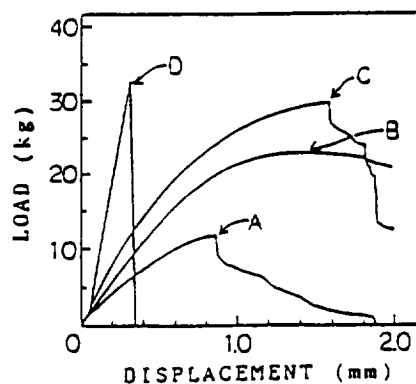


Fig. 7 Load-displacement curve for CMC using Si-Ti-C-O fiber at 1400°C in air.
A: plane web
B: UD sheet
C: UD sheet + powder
D: Si-Ti-C-O powder

COMMENTS REGARDING CMC EFFORTS IN JAPAN

The approach and expectations for CMCs in Japan differ from those in the United States. Our overall goals are set in part by various separate funding agencies, which are essentially striving for major "breakthroughs" in processing or performance capabilities. Entrepreneurs, inventors, discoverers, or developers have opportunity and reasonable chance of influencing the system and receiving support to bring their work to an evaluation-demonstration stage.

In Japan, through MITI/AIST, there is major top-down study, planning, and direction of how to deploy the national technical resources to the best advantage. The various organizations compete for performing the required work. This results in the parcelling of responsibilities and delineation of the approaches to be pursued at a given facility. The work is reviewed by committees of experts drawn from the entire technical community. In addition, the work is presented at annual meetings open to all interested and participating organizations. This approach is efficient in terms of information exchange and maximizes the overall effort on a given goal. The disadvantage is that there is relatively little opportunity for dissent or totally new concepts to emerge at the "grass-roots" research level. For example, there was notable convergence regarding which CMC systems to study, but no discussion of the probable critical barriers to meeting the intended turbine or HST/SST requirements and no discussion of other CMC systems that might offer reasonable alternatives to satisfying the requirements. However, the JTEC panel did see creative, elegant, and well-thought-out approaches to solving or supporting the main goal.

There appears to be a consensus that enhancing the toughness of the best available structural ceramics is the appropriate path. Even though Japan is a prime supplier of continuous high-temperature filaments (e.g., Nicalon, Tyranno, and Sumitomo fibers) that fuel much of the CMC research effort in the United States and Europe, the Japanese CMC effort has largely ignored these filaments and concentrated instead on particulate or whisker SiC and Si_3N_4 reinforcements. This decision apparently is based on the fact that the continuous filaments degrade under the processing conditions needed to incorporate them into SiC or Si_3N_4 , which have been selected as the preferred ceramic matrices. All of these whisker and continuous reinforcements are already commercial products. The strengths of Japan in the production of the above whiskers and in ceramic processing can be exploited in the making of high-performance ceramic cutting tools and high-temperature structural composites.

If better reinforcements are to become available, this will be the result of development by the companies that would be interested in such fibers as a commercial venture, and not as a result of a governmentally defined goal. That is, the approach is *to work with and to perfect what is available and economically*

viable rather than to search for the ultimate material or product for which the total demand may be so limited that its production requires subsidy.

The long-term planning and funding of the AIST programs provides for stability and maximizes the potential for a successful conclusion to the work. The competition between the various GIRs for significant portions of the work appears to result in considerable variation in the investment in facilities and equipment. The approach to the research that the JTEC panel saw was experimental and tended to be pragmatic and phenomenological rather than shaped by theoretical concepts or focused toward computer models. The staffs all appeared to be competent, and most of the personnel were highly motivated and clearly proud of their work. There were a number of examples in which the work and approach were outstanding.

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CHAPTER 4

METAL AND INTERMETALLIC MATRIX COMPOSITE RESEARCH AND DEVELOPMENT IN JAPAN

John H. Perepezko

INTRODUCTION

Japan's entry into metal matrix composites (MMC) occurred about a decade later than that of the United States and Europe; however, the Japanese have more than made up for any lost time in all aspects of composites, including fiber production, composite development, materials processing, design, production, and most importantly, commercial applications. A major increase in Japanese activities in advanced metal matrix composites started in 1981 with a project of the Ministry of International Trade and Industry (MITI) entitled the Advanced Composite Materials (ACM) Project. Indeed, the MITI-sponsored ACM project may be viewed as an attempt to compensate for the absence in Japan of the military aerospace efforts that were responsible for much of the U.S. and European composites activity. This composite effort was also designed to match more closely with the traditional approach in Japan to focus on the development of advanced materials for a commercial market rather than [for] a military application. Along with this approach was the overriding attention to cost-effective production with adequate materials performance rather than the typical military approach of maximum performance at relatively high cost. As with most of MITI's "Large-Scale" research and development products, the ACM project which ended in 1989 has been claimed a success.

With the completion of [the] MITI project in advanced composites, there has been a review by a team from the United States (Ref 4.1). For completeness some of the high points of this program will be included in this [the following] discussion.

Unfortunately, the visit sites that were selected were not ones with a current high level of activity in metal matrix composites; in fact, the expiration of the MITI ACM program appears to have coincided with a change in emphasis throughout Japanese industrial and government research labs to reduce the research effort on conventional metal matrix composites. At present, MMC research in Japan is essentially in a holding pattern: products have been produced, but not necessarily in the most cost-effective manner. Almost all current activity is focused on further reducing cost and/or finding applications for existing products.

Following the [completion] of the MITI ACM program, a new effort has recently been launched in the area of intermetallic matrix composites and other high-temperature materials intended for aerospace applications; in particular, for use in hypersonic transport vehicles. These developments appear to be a clear result of the top-level decision in Japan to become a leading contender in the aerospace industry in the future. The efforts in this area are relatively new; as a result, there was relatively little in terms of new developments that were available during the JTEC panel's visit. Much of the summary of these activities is based upon projections and goals, although some limited but important successes have already been achieved in the area of high-temperature materials.

It is important to note that in all aspects of high-temperature materials and composites research, the prevailing view in Japan is that this activity is a long-term investment involving periods of ten years or more before any applications are anticipated to be demonstrated on a large scale. This viewpoint can be anticipated when it is considered that most of the project development at MITI is planned by scientists and engineers rather than being controlled by accountants.

MITI'S ADVANCED COMPOSITE MATERIALS PROGRAM

In any discussion of Japanese MMC activities it is important to consider the MITI initiatives, because these are viewed with such high regard by industry, government, and university research groups. The MITI advanced composites project under "Basic Technologies for Future Industries" focused on composite materials between 1981 and early 1989. The project was promoted by MITI's Agency of Industrial Science and Technology (AIST), with the participants and organization shown in Figure 4.1. The companies participating in this joint venture also acted as members of the Institute of Materials and Composites for Future Industries. Carbon fiber reinforced plastics were also included in the project, but are not discussed in this report.

The purpose of the ACM program was to develop moderately high performance structural materials using continuous fiber reinforcement for potential structural applications and future automobile and large aircraft structures (Refs. 4.1-4.3).

Much emphasis was given to application of fibers developed and produced in Japan, such as carbon fiber and SiC fiber. The main properties of the composites to be developed (referred to in Japan as fiber-reinforced metals [FRM] rather than as MMC) were targeted as follows:

1. Thermal Resistance: temperatures up to 450°C with retention of 90% of room temperature strength
2. Tensile Strength: over 150 kg/mm² at room temperature.

These targets were achieved for wire preforms, as indicated in the data in Table 4.1, which comes from a summary report of the MITI project (Refs. 4.2, 4.3).

A major trend in Japanese FRM research and development has been its focus on short (i.e., discontinuous) fiber-reinforced composites intended for functional applications such as wear resistance. The development of continuous fiber-reinforced metal composites for structural applications was relatively less active until the MITI project. The main achievement has been in the development of materials and the fabrication of test pieces to provide for an evaluation of strength. Scale-up of fabrication and practical applications remain to be determined.

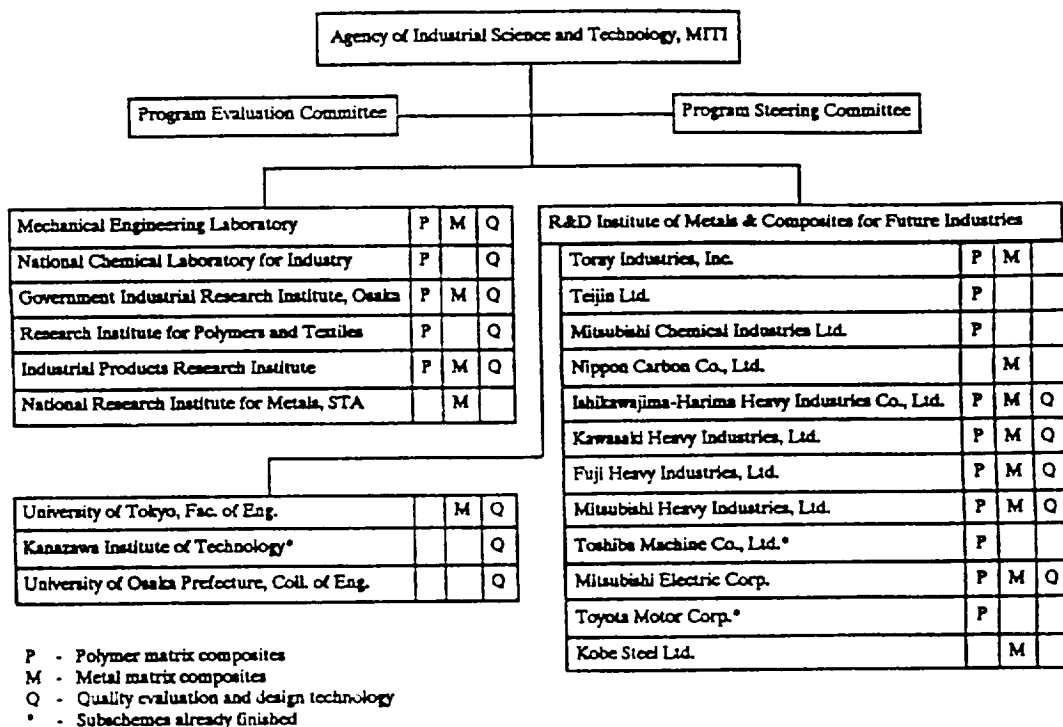


Figure 4.1. Organization of the Advanced Composite Materials (ACM) program detailing areas of research.

Table 4.1

		FRM		
Material		Target	SiC(NICALON) / Al - 5.7Ni $V_f = 50\%$ Wire	SCS - 6 / Ti - 6Al - 4V $V_f = 50\%$ Sheet
Temperature		Room Temp.		
Tensile strength	Average (MPa)	–	1692	1988
	B value (MPa)	1470	1550	1523
Temperature (K)		723		
Tensile strength	Average (MPa)	–	1689	1769
	B value (MPa)	1320	1512	1664

B value: Lower limit of reliability of 90% by statistic
analysis of measured data

SCS - 6: SiC (CVD) fiber made by AVCO

FRM Fabrication R&D in Support of ACM Project

A great deal of the research in composites has been directed towards fabrication technology; in particular, towards the initial processing production methods. The main methods that have been developed are illustrated in Figure 4.2 and include hot pressing, hot rolling, hot isostatic pressing (HIP), and pressure casting or squeeze casting (Ref. 4.1). The most attractive fabrication method is pressure casting because of (a) relatively low fiber damage, good melt infiltration, and applicability to poor wetting conditions; (b) short cycle time which is appropriate for mass production; (c) relatively low cost of capital equipment; and (d) the capability of incorporating higher fiber volume fractions than other methods. Comparison of the various fabrication methods is shown in Table 4.2 and emphasizes that the development of squeeze casting as a viable economic production route was an important development of the MITI ACM program.

A good example of the excellent research on squeeze casting methods comes from the work of Dr. Yamada at the Nippon Steel Research Center (seen on a visit arranged independently of the JTEC visit schedule) (Ref. 4.4). As indicated in

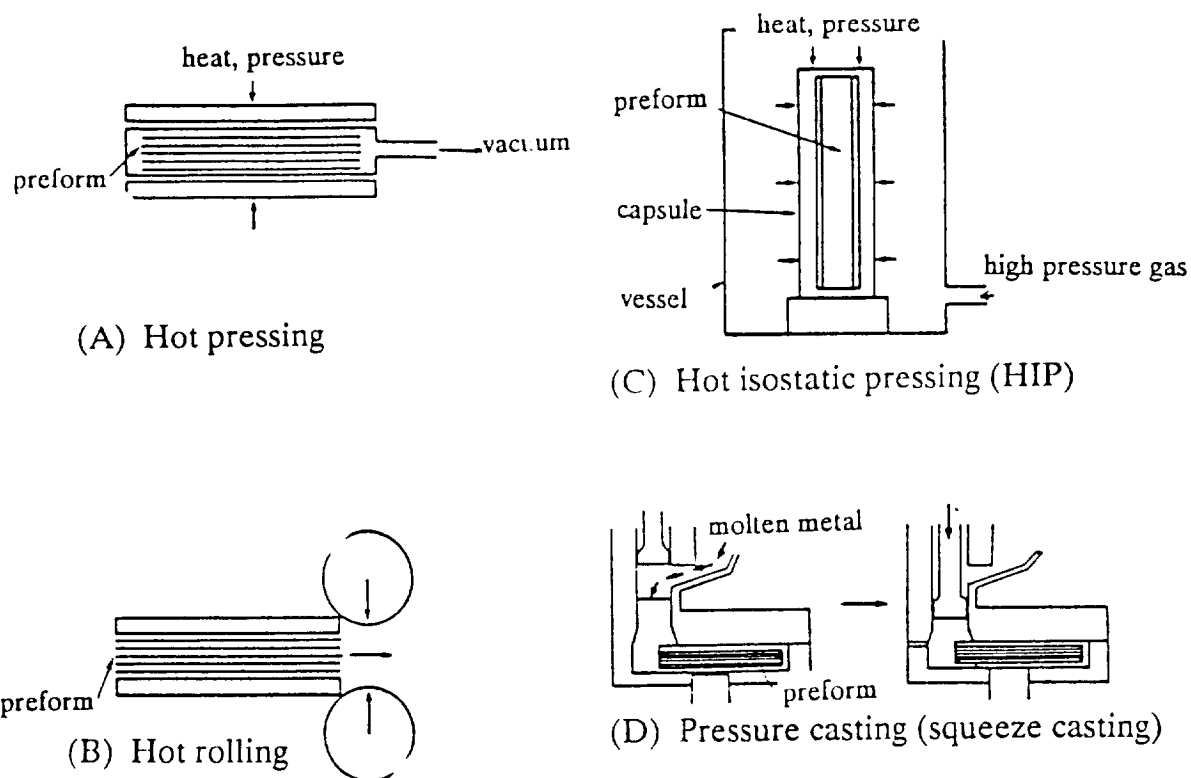


Figure 4.2. Main methods of forming FRM

Table 4.2
Comparison of FRM Fabrication Methods

Principal Methods	Fiber Damage	Reaction w/ Matrix	Void in FRM	Cycling Time	Cost
Hot Pressing	G	E	G	B	G
Hot Rolling	B-G	E	G	E	E
Hot Isostatic Pressing (HIP)	G	E	E	B	B
Pressure (Squeeze) Casting	E	E-G	E	E	E

E: Excellent; G: Allowable; B: Not Good

Figure 4.3, the development of a squeeze casting process includes an environmental control through a vacuum vessel for degassing, the provision for means of agitating the melt so that in the semisolid state grain refinement can be produced which allows for a uniform dispersion and incorporation of the various fibers which are mainly silicon carbide. Also by careful control of the temperature-time thermal history cycle to pinpoint periods of reinforcement addition and final casting, a uniform dispersion with a high volume fraction of fiber is possible (Fig. 4.4).

Although the aluminum alloy matrix composites achieve the MITI set goals at room temperature, in almost all cases there is a deterioration of strength at elevated temperature where a rapid dropoff occurs at temperatures above 250°C (Fig. 4.4). At least part of the reason for this dropoff in strength is related to the development of an interfacial reaction between silicon carbide and the aluminum alloy melt to form an aluminum carbide. As shown in Figure 4.5, there is some control possible over the amount of reaction product, but complete removal is not feasible within the constraints of cost-effective production.

With the development, at least at room temperature, of adequate mechanical properties with aluminum alloy matrices, there has been relatively little effort to examine the interfacial reaction between the matrix and SiC. Instead, effort has focused on optimizing the squeeze casting process and examining modifications in aluminum matrix chemistry. However, at the Osaka Government Industrial Research Institute (GIRI) an interesting approach to fiber-matrix reactions is being taken by K. Honjo. In this case, carbon fibers in aluminum are under investigation (Refs. 4.5, 4.6). The interfacial reaction produces Al_4C_3 , but again, the kinetics are not extensively studied. Instead, coatings involving 0.2 μm of TiN or SiC are placed on the carbon fiber as diffusion barriers and to aid in improving wettability. Also, as indicated in Figure 4.6, a carbon undercoat between the diffusion barrier and the carbon fiber is used to promote a healing of any defects in the original carbon fiber and to provide a weakly bonded interface that provides a path for crack deflection and arrest by debonding, leading to improvement in fracture toughness of the composite. This novel approach employs some of the more advanced micromechanic concepts for improving toughness of composites (Ref. 4.7). However, since these additional coatings increase the complexity of production and cost of component manufacture, industrial interest has been slight.

The strong emphasis on cost-effective applications has led some of the other research to focus on alternate fibers. At the Nagoya GIRI, an effort by Dr. Nishida to examine potassium titanate fibers for use in squeeze casting of aluminum FRM is underway (Refs. 4.8, 4.9). The whiskers are 10-20 microns in length with an aspect ratio of about 10. Although the whiskers do not have the same stiffness or wear resistance as SiC, $K_2O \cdot 6TiO_2$ does provide for an adequate strengthening, as indicated in Figure 4.7. The $K_2O \cdot 6TiO_2/Al$ FRM are intended for use in components

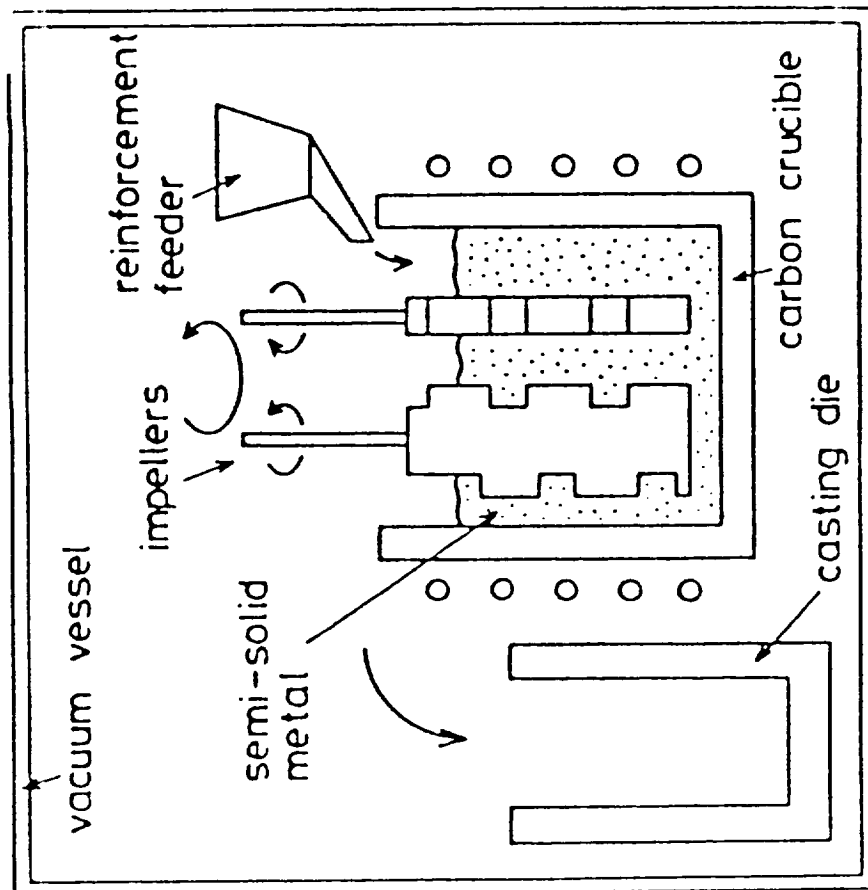
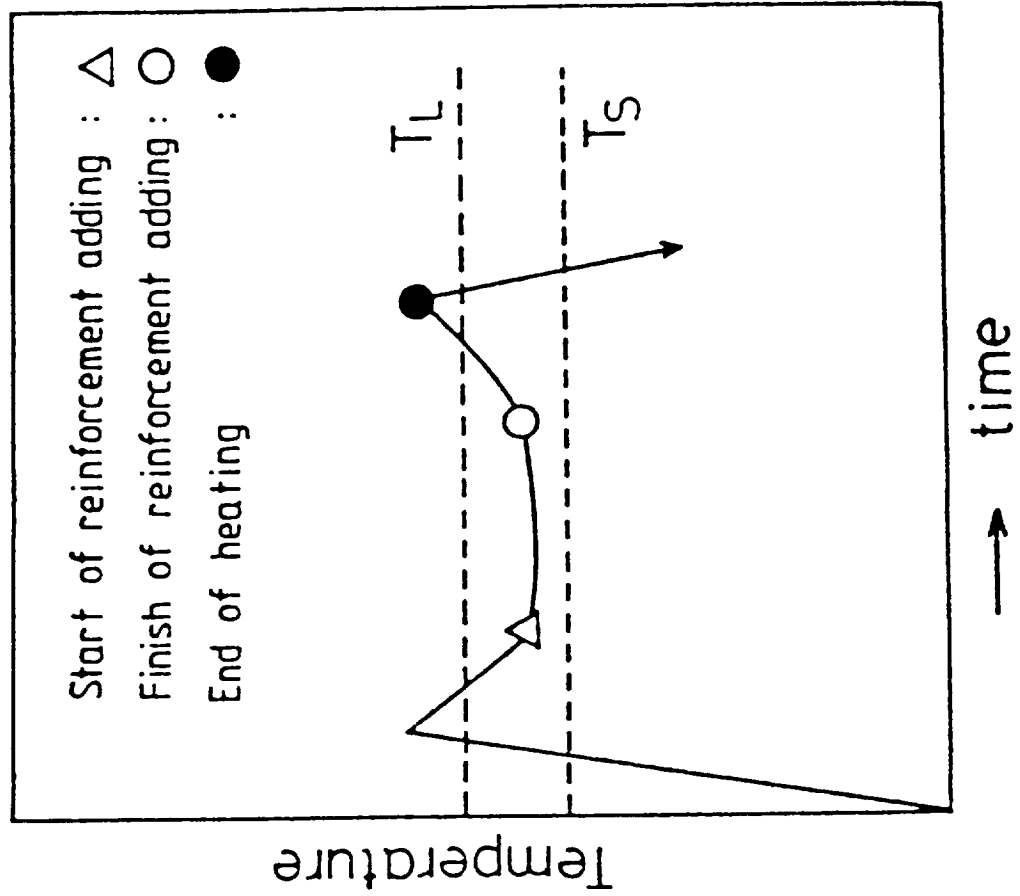
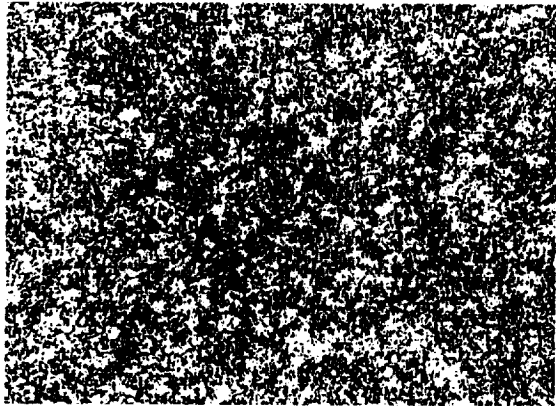
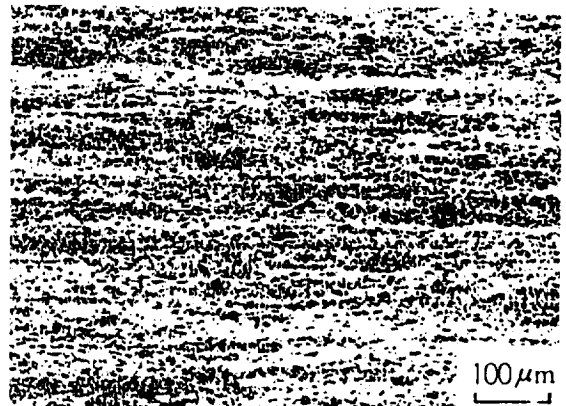


Figure 4.3. Squeeze casting process for FRM fabrication.



Billet

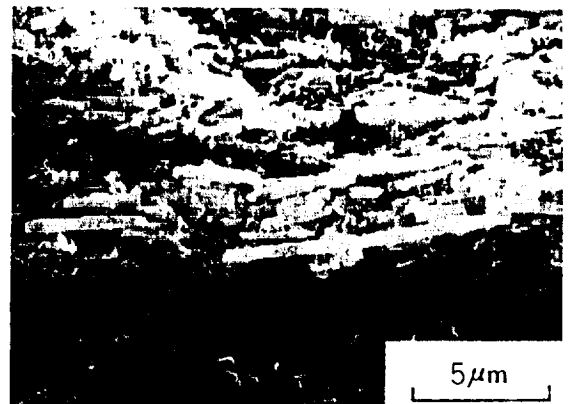


Extruded rod

a) optical micrographs of 20% SiC whisker / 6061 Al composite



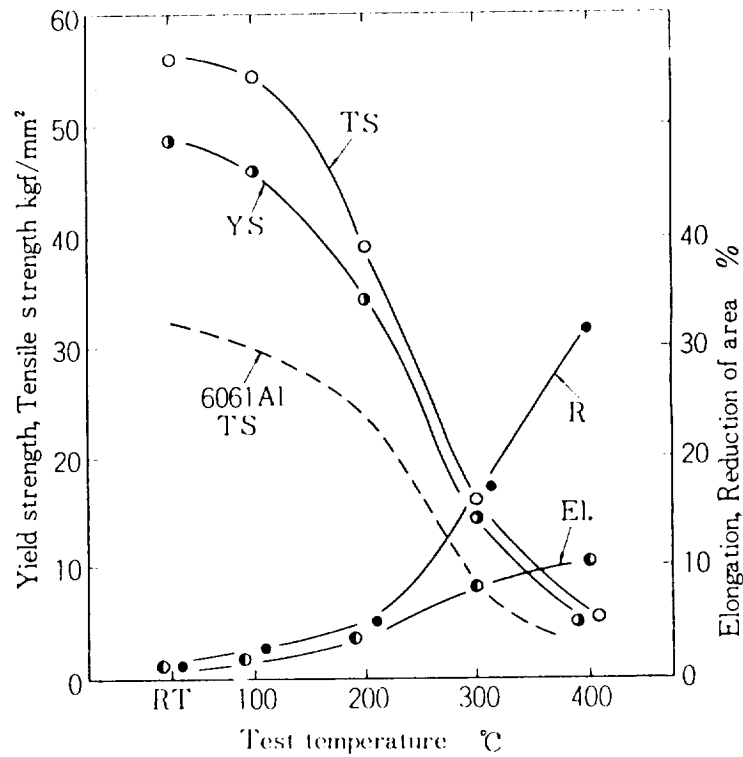
Billet



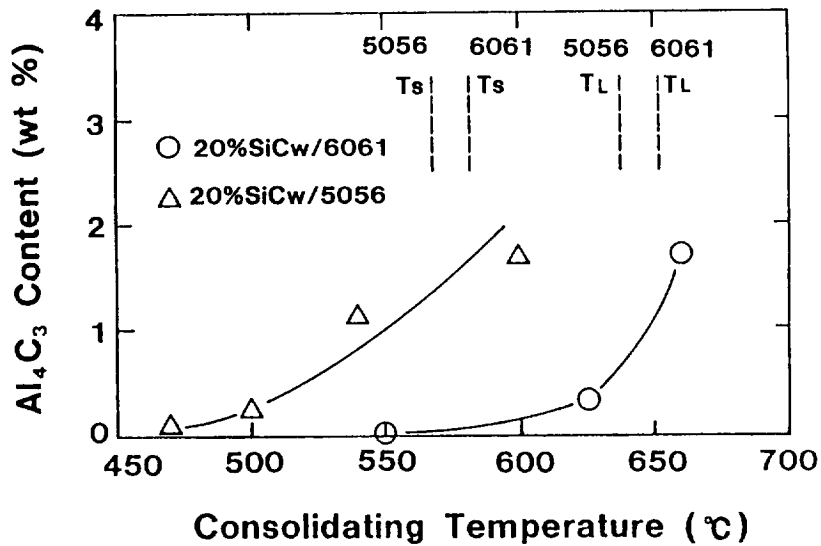
Extruded rod

b) SEM micrographs of 20% SiC whisker / 6061 Al composite

Figure 4.4.



(a) Tensile properties of 20% SiC whisker/6061 Al composite at elevated temperatures (T1 extruded rod).



T_s : Solidus line temperature T_L : Liquidus line temperature

(b) Relationships between consolidating temperature and Al_4C_3 content for 20% SiCw/6061-T6 & 20% SiCw/5056 composites.

Figure 4.5.

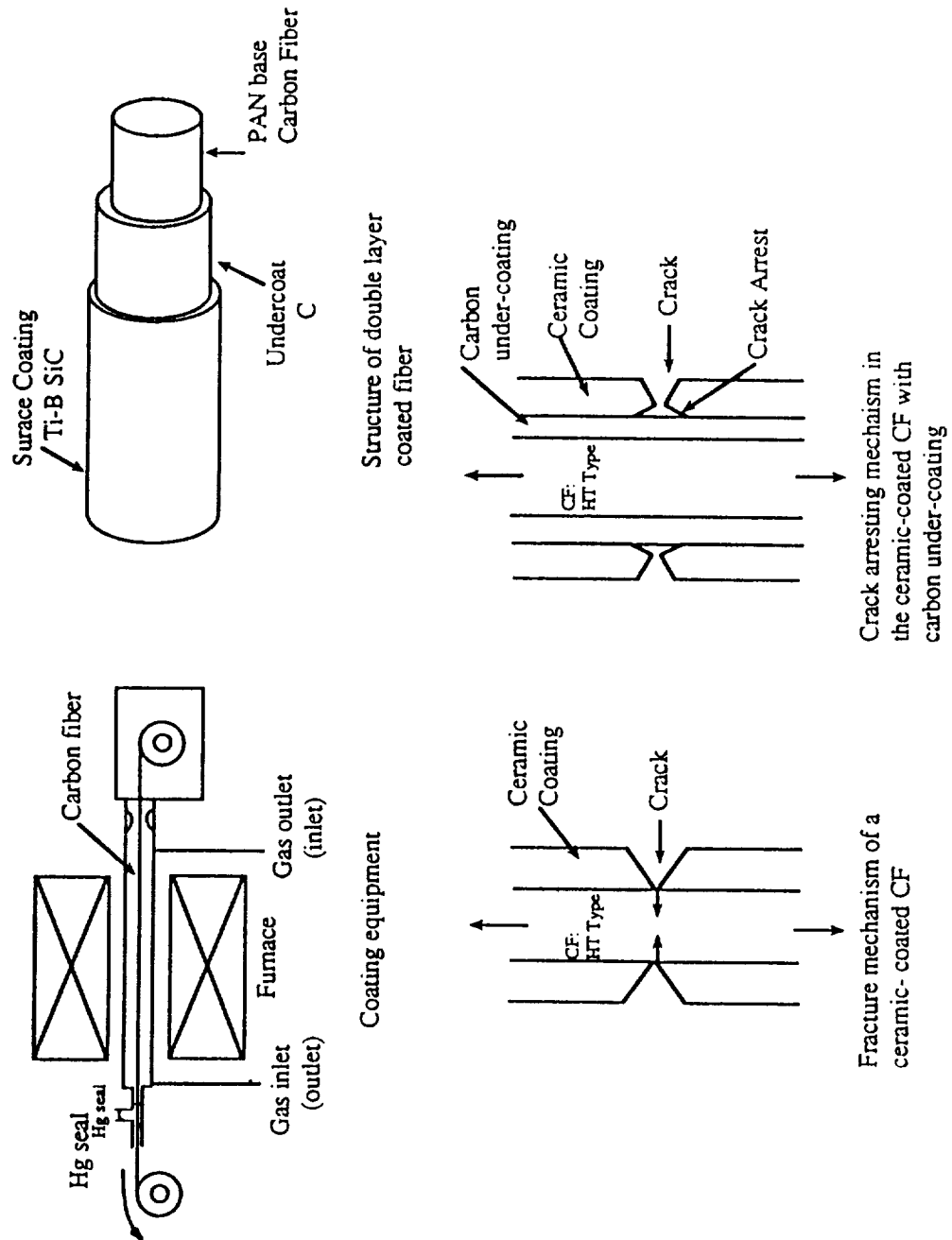


Figure 4.6.

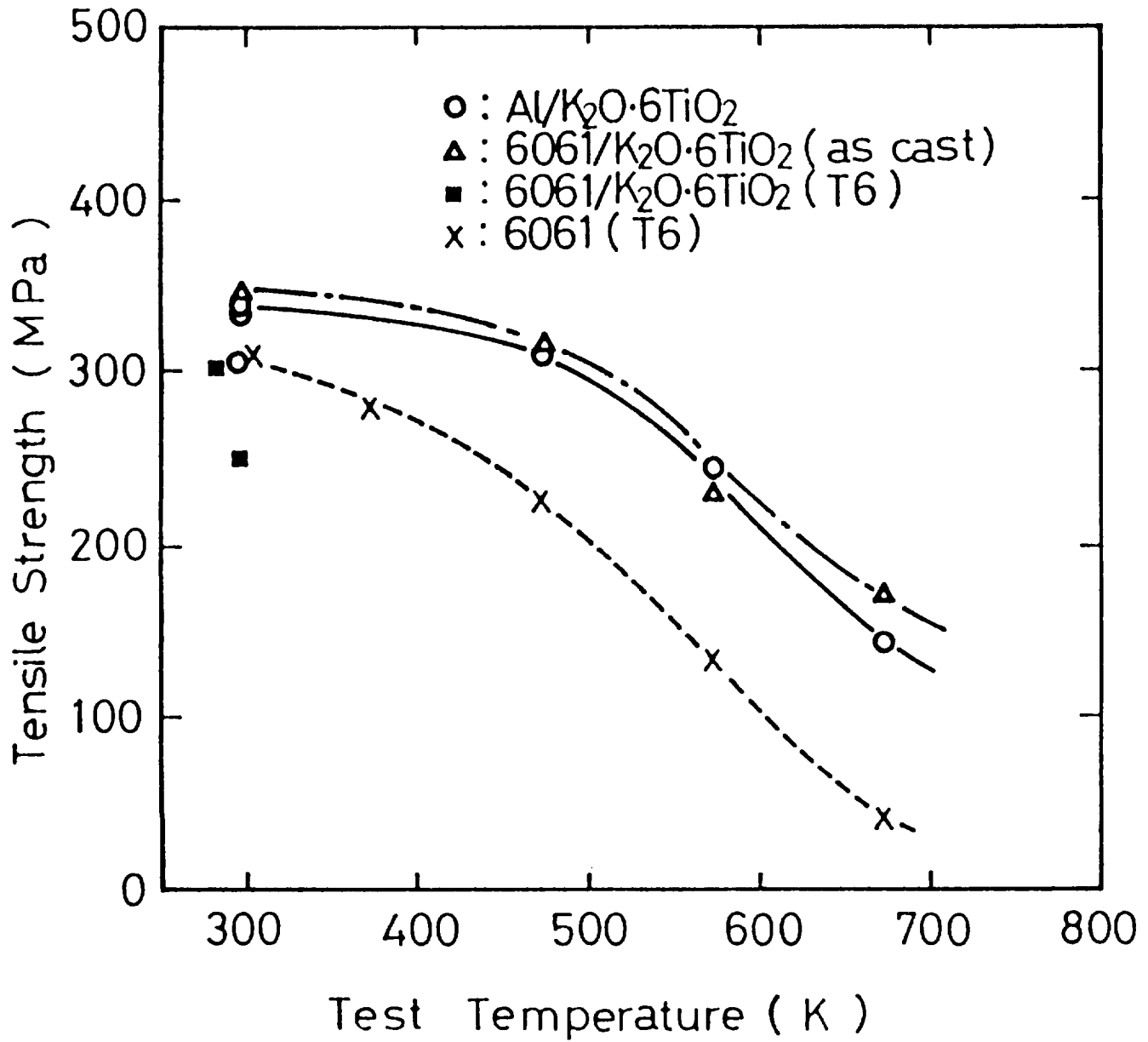


Figure 4.7. Tensile strength of the composites and 6061 alloy.

where ease of machinability can be an important factor. The main advantage is that the whisker is of low cost--approximately one-fiftieth of the cost of SiC whiskers. The strength of composites based on the potassium titanate whisker also diminishes above 250°C and is sensitive to processing in terms of the thermal stability of the whisker, but the processing has been optimized to accommodate this problem. Other fiber materials that are being studied include aluminum borate (Ref. 4.10) and Si₃N₄ (Ref. 4.11).

In other locations such as a Kawasaki Heavy Industries (KHI) (Ref. 4.12) and Kobe Steel (Refs. 4.13-4.15), the progress in aluminum matrix FRM has been similar, and desirable mechanical properties have been successfully attained. At least some small test components have been fabricated and prototype structural components and thin wall tubes have been demonstrated (Refs. 4.12, 4.14). However, commercial applications that would warrant large-scale production have not been forthcoming, especially from the automotive industry. As a result, a decision has been made to devote some attention to attempting to further reduce cost but to devote little attention to any further performance improvements.

For intermediate temperatures up to 450°C, the mechanical performance goals have been met by titanium alloy matrix FRM. Typical of the effort in this area is the work of K. Aota at Kobe Steel (Ref. 4.15). Examples of the types of titanium alloy matrices examined are shown in Figure 4.8, and a flow chart indicating the processing method is shown in Figure 4.9. A powder sheet is combined with a filament mat to form a laminate structure that is encapsulated and then finally consolidated by HIP treatment. The use of a HIP process is not unexpected at Kobe Steel, since it is the main producer of HIP units in Japan and one of the world leaders in this area. With a volume fraction of 38% silicon carbide, the strength levels in most of the titanium matrices have been established at or above the MITI goal levels. Again, some interface reaction has been noted, but since the target of properties has been achieved at temperature, this has not caused great concern. In fact, the target properties represent a 150% improvement over a nickel base system such as Incoloy 800, as indicated in Figure 4.10.

Many of the activities at the different industrial and government laboratories overlap to a considerable degree--similar approaches on similar materials are being pursued. Apparently, this is an intention on the part of the MITI program and one in which the Japanese achieve rapid progress in a very focused area. This is often called the parallel approach and is perhaps one of the reasons for the rapid Japanese advancement in the squeeze casting processing of aluminum FRM. The drawback of this approach is the limited number of options that can be explored and the early decision that must be made on a final processing route.

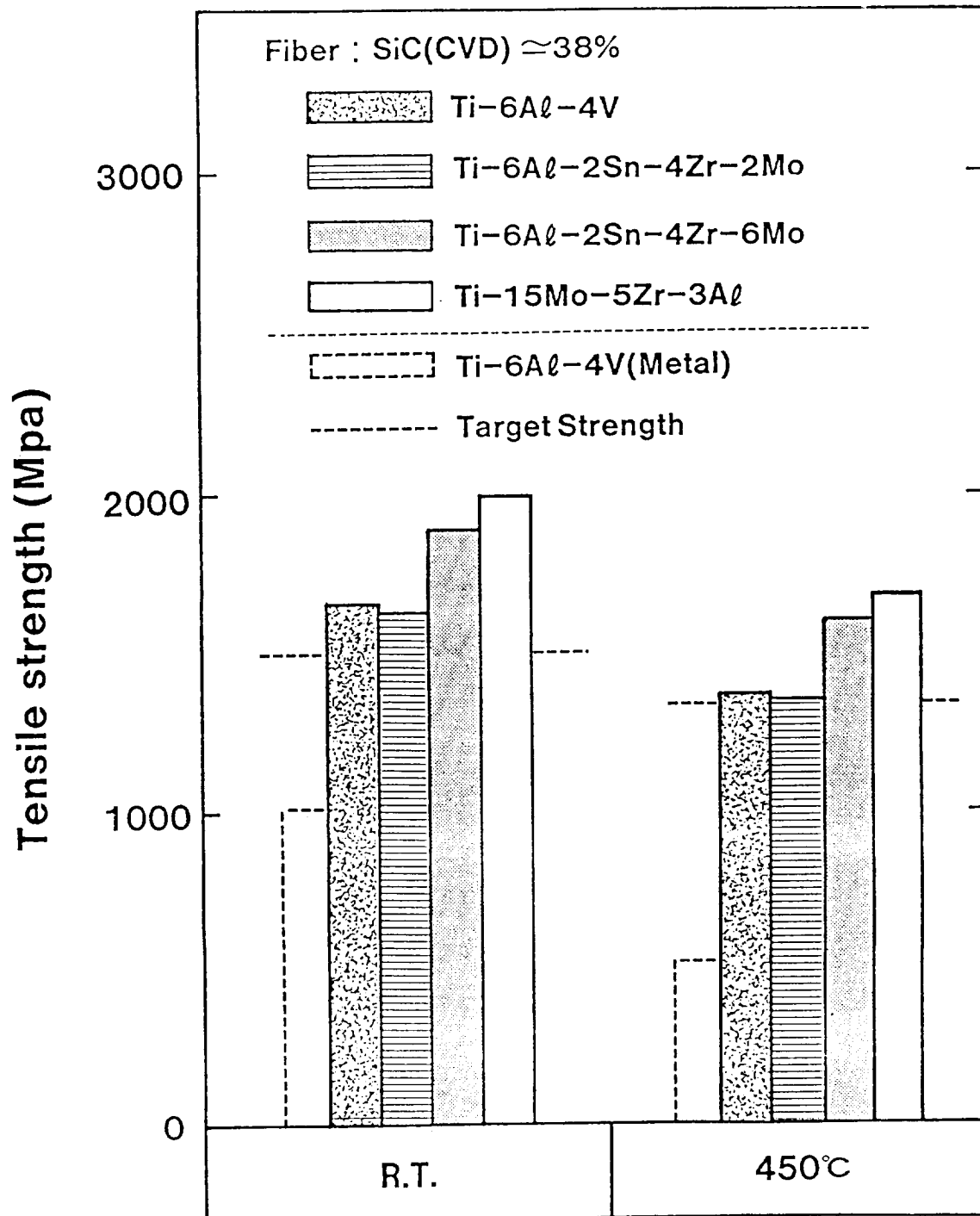
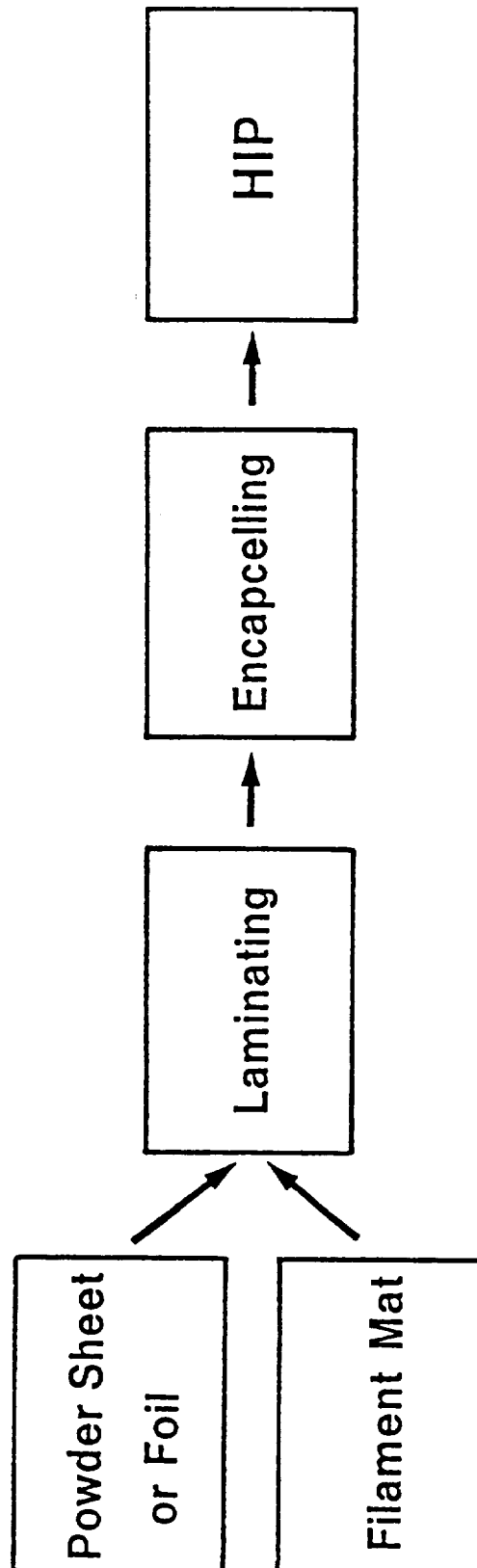


Figure 4.8. Effects of the matrices on tensile strength of P/M Tibase - FRM



(Powder sheet : useful for the matrices unobtainable in the foil shape)

Figure 4.9. Process of Ti base - FRM by HIP

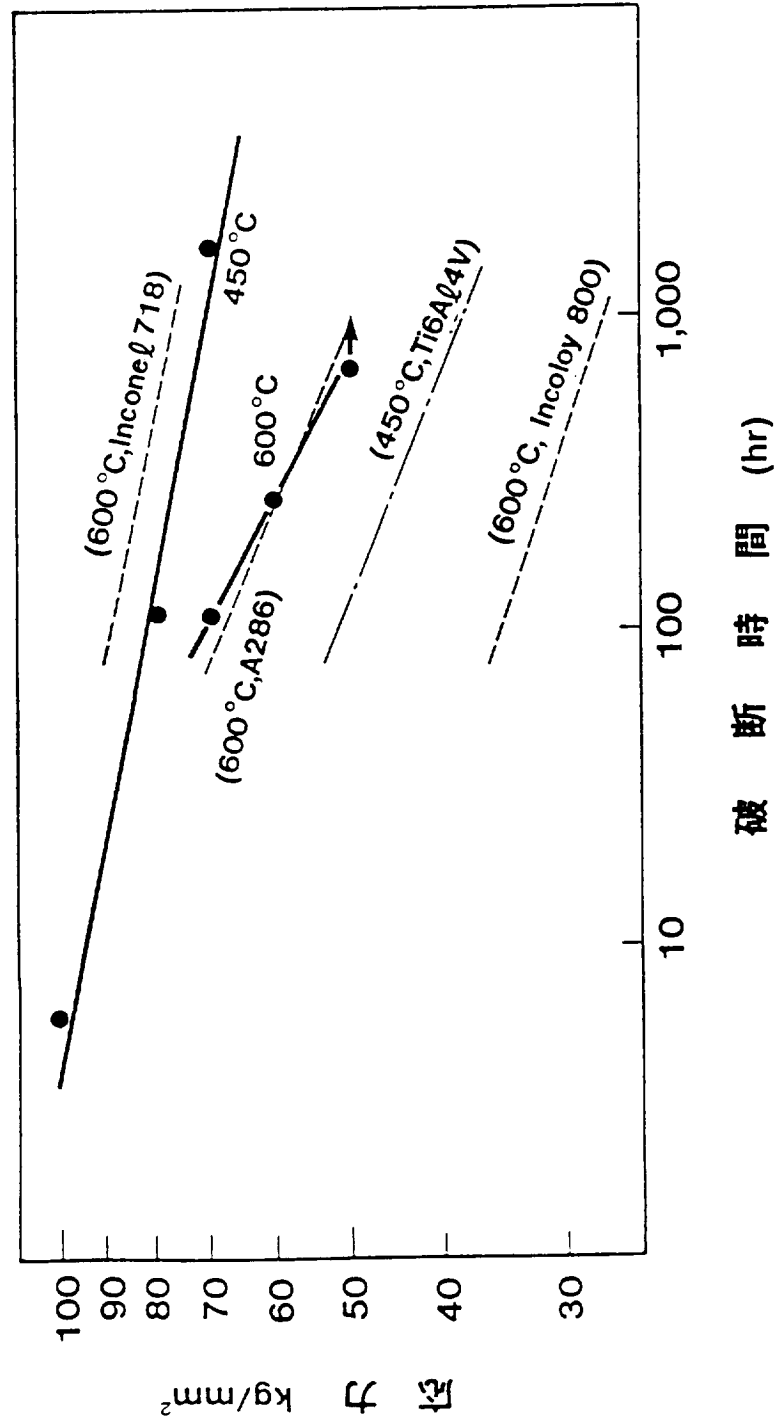


Figure 4.10. Creep rupture strength of SiC(cvd)/Ti-15Mo-5Zr-3Al.

MITI INITIATIVE IN HIGH-TEMPERATURE MATERIALS

In mid-1989, MITI/AIST initiated a new project under the Basic Technologies for Future Industries program entitled "High Performance Materials for Severe Environments." The duration of this project is 8 years. Its main purpose is the development of high-temperature-resistant structural materials for aerospace applications, including both engine and structural components (Ref. 4.16). One intention is to develop materials for the Japanese spaceplane Hope*, shown in Figure 4.11, and for high-speed transport, as shown in Figure 4.12. The materials should be suitable for a prototype engine at the termination of the project. Of particular interest in Figure 4.12 are the domains indicated for the temperature regime where intermetallic matrix composites and functionally gradient materials (FGM) are situated.

Although the JTEC panel's visit schedule did not include any sites with extensive activity in intermetallic matrix composites, there was an important development at KHI by H. Nakayama and Dr. Fujioka on monolithic intermetallic alloys. In particular, TiAl is under extensive investigation as a suitable material for turbocharger applications (Ref. 4.17). The reason for this is shown in Table 4.3, where the properties of TiAl are compared with Si_3N_4 ceramic and nickel base superalloy.

Table 4.3
Physical Properties of TiAl, Si_3N_4 , and a Ni-Base Superalloy

	TiAl	Ceramic* ¹	Metal* ²
Density (g/cm ³)	3.8	3.2	7.9
Thermal Conductivity (cal/s·cm·K)	0.05	0.07	0.03
Thermal Expansion ($\times 10^{-6}$ /K)	10.3	2.8	13.1
Young's Modulus (kgf/mm ²)	17600	31600	22400
Poisson's Ratio	0.28	0.24	0.30
Fracture Toughness (kgf/mm ^{3/2})	42	19	239

*1 : Silicon Nitride (Si_3N_4)

*2 : Ni Base Superalloy (Inconel 713C : Ni-13Cr-4Mo-6Al-0.7Ti-2Nb-0.01B)

* MITI states that this project is aiming at materials research for the large high speed transport market, in which HOPE *might* be included.

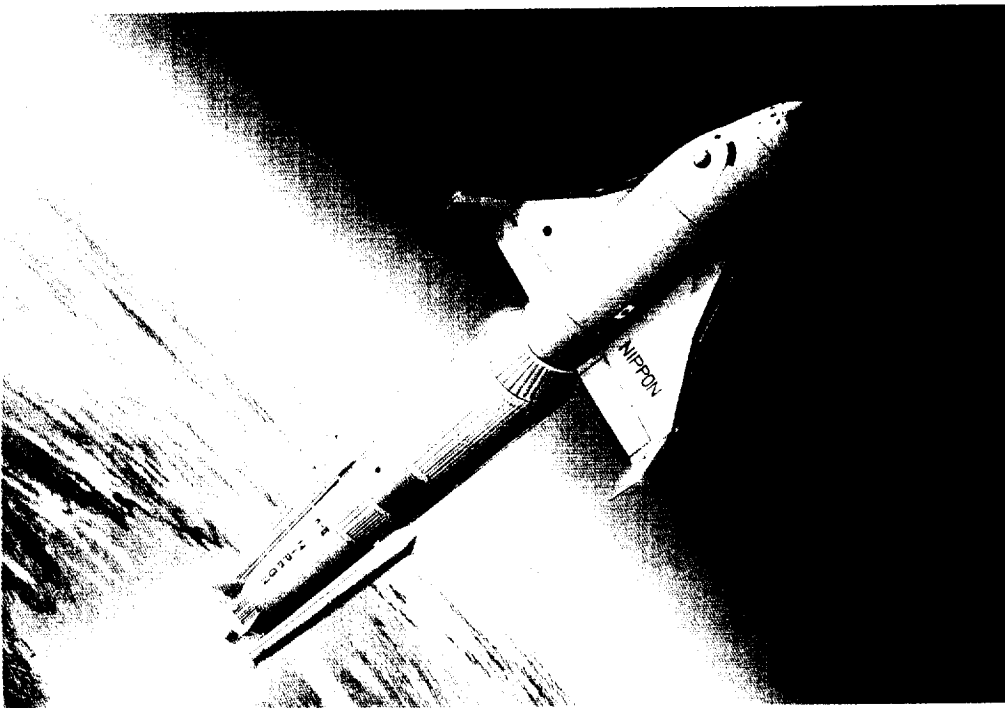


Figure 4.11. Japanese spaceplane "Hope."

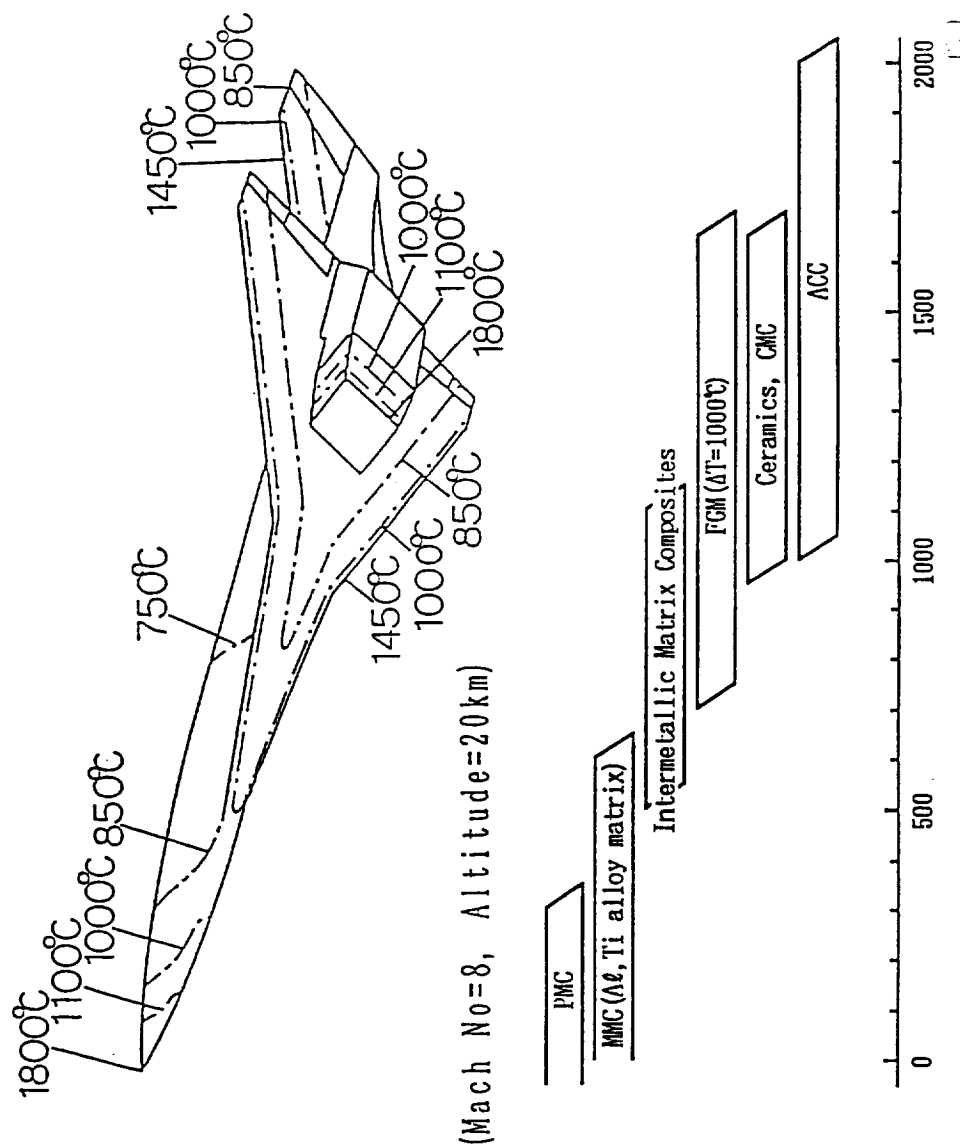


Figure 4.12. Service temperature of various materials.

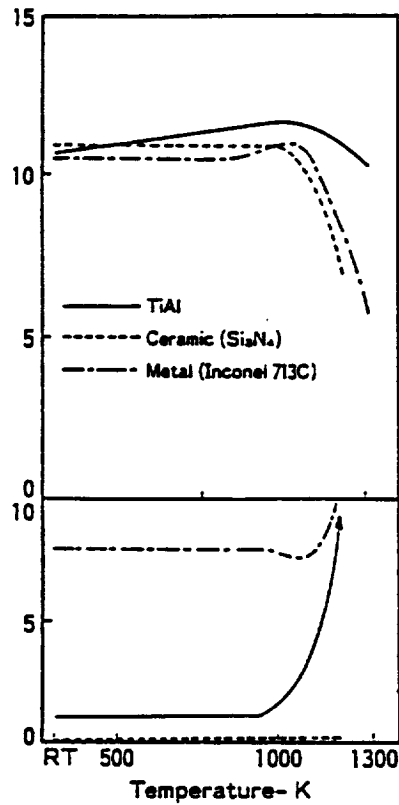
The advantage of TiAl is that it has a density comparable to the ceramic, which is about half that of the metal, with high modulus and expansion coefficient comparable to metals. The high-temperature properties in terms of oxidation and creep rupture are favorable for TiAl when it is coated. Most important, however, is the transient response of a TiAl, as shown in Figure 4.13, where the low density allows for increased response at much higher turbine speeds and temperatures than nickel base alloys. With proper treatment TiAl also has adequate toughness. These characteristics yield an important enhancement of performance of almost 20%. The main production route is an investment casting procedure where alloy chemistry is carefully controlled to yield suitable mechanical properties. Certain additives such as nickel and boron are believed to contribute to the useful ductility of the material ($\sim 2\%$ at room temperature). With this application and commercial demand established, the current attention of activities at KHI is on coatings and on further improvement in cost-effectiveness in manufacturing. Based upon the enthusiasm and interest in these materials, it is likely that aluminides will grow in importance. From this basis with the monolithic material, composite work is likely to develop in the near future.

FUNCTIONALLY GRADIENT MATERIALS

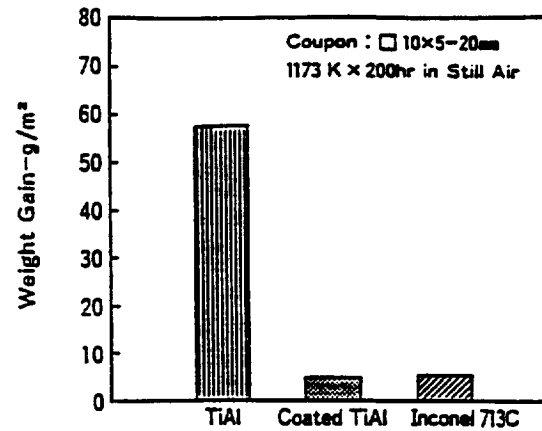
A functionally gradient material does not have a uniform distribution of structure and properties. Such materials have existed for some time, especially in connection with various coatings and surface treatments. A systematic approach to investigating these materials has been promoted in Japan since 1989 by AIST under the auspices of the High Performance Materials for Severe Environments Project in order to develop materials for relaxing thermal stresses (Ref. 4.18). The expected applications are thermal insulating and thermal protecting materials for aerospace structures (Ref. 4.19). In particular, the main applications driving this work are the Japanese spaceplane and the HST (hypersonic transport). At present the FGM activities are at a high level, occurring in almost every one of the laboratories that the JTEC panel visited; Japanese FGM work is widely regarded as being in the basic research stage. The third international conference on FGM was held in Japan this year.

The following discussion on FGM developments is based solely on information obtained during the JTEC panel visit to Japan, because the panel was unable to obtain FGM literature in translation within the timeframe of this report.

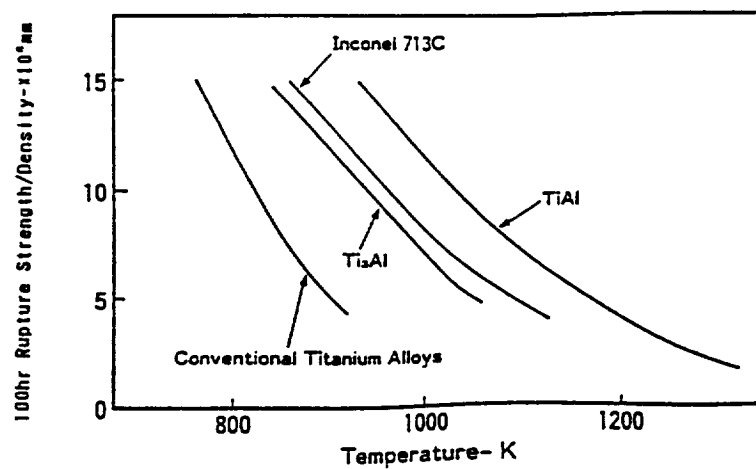
The concepts behind the FGM strategy are illustrated in Figures 4.14 and 4.15, where the bonding between a metal and ceramic is accomplished over a graded layering with no steep, sharp discontinuity. With this approach, the development of thermal stresses is relieved. In addition, other additives and controlled porosity



Tensile Properties



High-Temperature Oxidation Resistance



Creep Rupture Properties

Figure 4.13. Properties of TiAl.

Durability and Acceleration Exceeding Ceramic Turbos'!

1. Unrivaled Quick and Sharp Response.
2. Ideal for Application to High-Performance Wheels.
3. Shockproof at Ambient and Elevated Temperatures.



Figure 4.14. Titanium aluminide turbo.

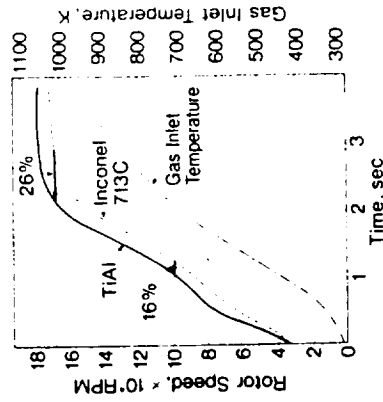
Physical and Mechanical Properties

Property	TiAl	Ceramics*	Metals
Density	3.8	3.2	7.9
Thermal Conductivity	20.9	29.3	12.6
Thermal Expansion	10.3	2.8	13.1
Young's Modulus	180	310	220
Poisson's Ratio	0.28	0.24	0.30
Fracture Toughness	13	6	73
UTS***			
at 300K	10.7	11.0	10.5
at 1173K	11.2	8.3	9.4
Elongation			
at 300K	1~2	0	6
at 1173K	5	0	7

* Si-Ni ** Ni Base Superalloy (Inconel 713C) *** Ultimate Tensile Strength

Transient Response of a TiAl Rotor

- **Turbine Wheel:**
Geometric Copy of
Inconel 713C Rotor
47mm in Tip Dia.
- **Test Facility:**
Hot Spin Test
Stand with
Kerosene Burner



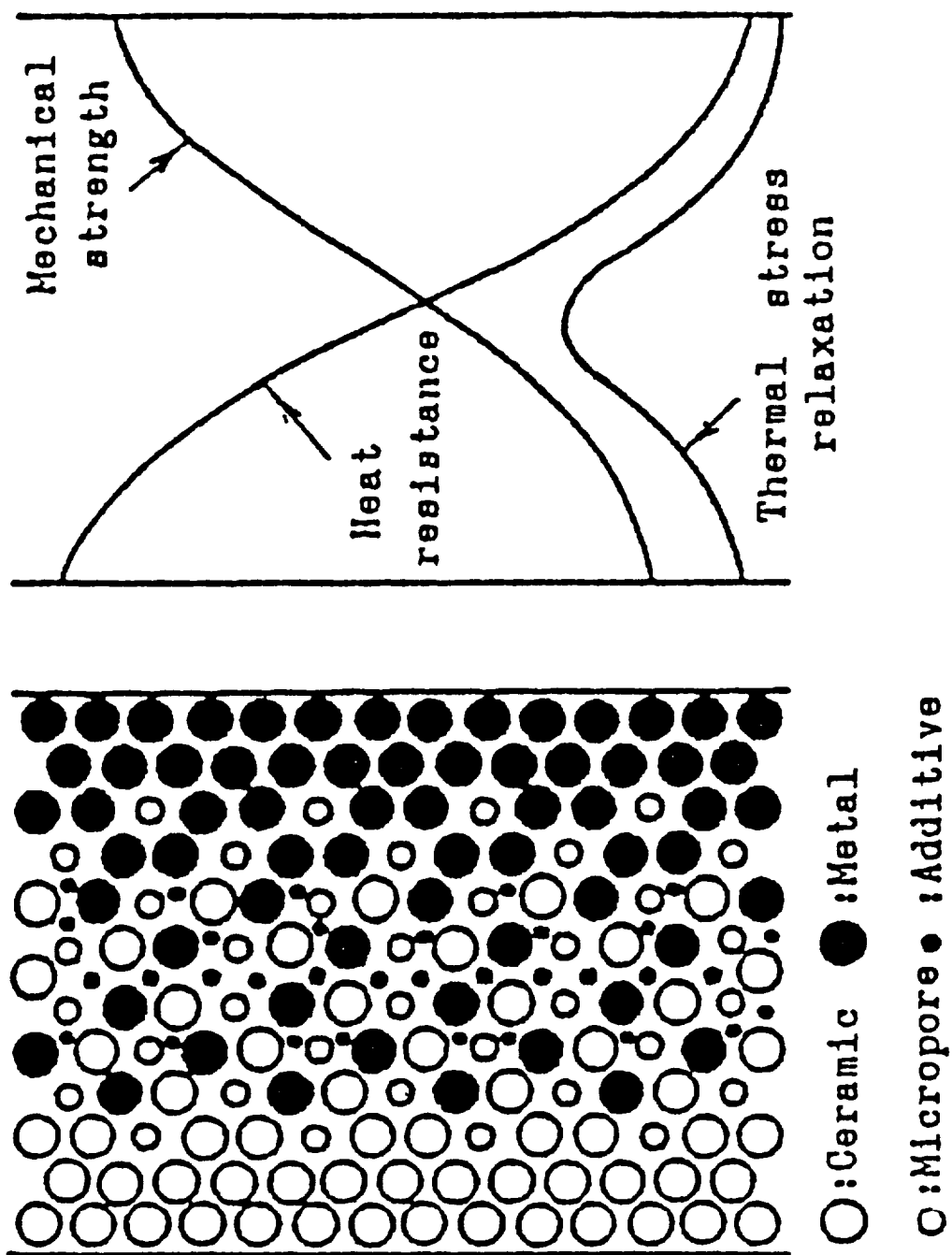


Figure 4.15. Concept of functionally gradient material.

can be used with this design to alter some of the characteristics of the graded layer. In effect, FGM is a monocomposite which is designed to control thermal stresses that are anticipated based upon thermal gradients that approach 10^3 °C per millimeter. As explained to JTEC panelists during their visit, the FGM program is not intended to develop new materials, but rather to combine materials in new forms to address the high levels of thermal stress and thermal cycling anticipated in advanced aerospace structures. One of the key concepts involved in the FGM program that is being pursued actively by Professor Watanabe in Tohoku University has been called "inverse design" (Refs. 4.18-4.22). Basically, this strategy has been developed to identify the applications that require a certain type of structure, and then work on the microstructure of the material. Usually with a more traditional strategy microstructural studies are done and based upon the particular characteristics of the microstructure, various design applications can be found. It is the panel's consensus that the FGM program is likely to have a large impact on the Japanese position for future dominance in the aerospace materials area.

As discussed separately in Chapter 3 on ceramic matrix composites, the processing activities behind the FGM program involve various powder metallurgy (PM) routes, in terms of both conventional PM processing and plasma spraying, pressure sintering of various components, and thermal gradient sintering where recognition is given to the fact that the ceramic and metal parts of a FGM monocomposite will require different sintering temperature treatments. The reactions involved in FGM production often also involve SHS (self-propagating high-temperature synthesis), due to the chemical reactions involved in forming the graded layers between the constituents. This poses a paradox in the sense that some chemical reaction is required in order to achieve effective bonding across the monocomposite of an FGM, but extensive reaction can cause degradation. Clearly, in high-temperature uses, reactions extending beyond the initial optimized configurations are likely to occur; however, the Japanese have not yet pursued extensive studies of high-temperature thermal stability.

Within the FGM program are several examples of the interaction between industry, university, and government industrial research institutes. For example, KHI and Osaka University have several programs, as summarized in Figure 4.16, dealing with FGM components through high-pressure combustion sintering involving the SHS reaction between intermetallics such as TiAl and MoSi₂, as well as a number of other ceramic and metal pairs. As indicated in Figure 4.17, by controlling the gradation scale and fineness and the number of gradation layers, it is possible to achieve a high degree of structural integrity. Plasma spraying is also used to produce these materials at the very finest levels of intermixing, where the graded layers may even be graded within each layer. There are other cooperative fabrication studies between KHI and the Government Industrial Research Institute in Sendai (Refs. 4.23, 4.24).

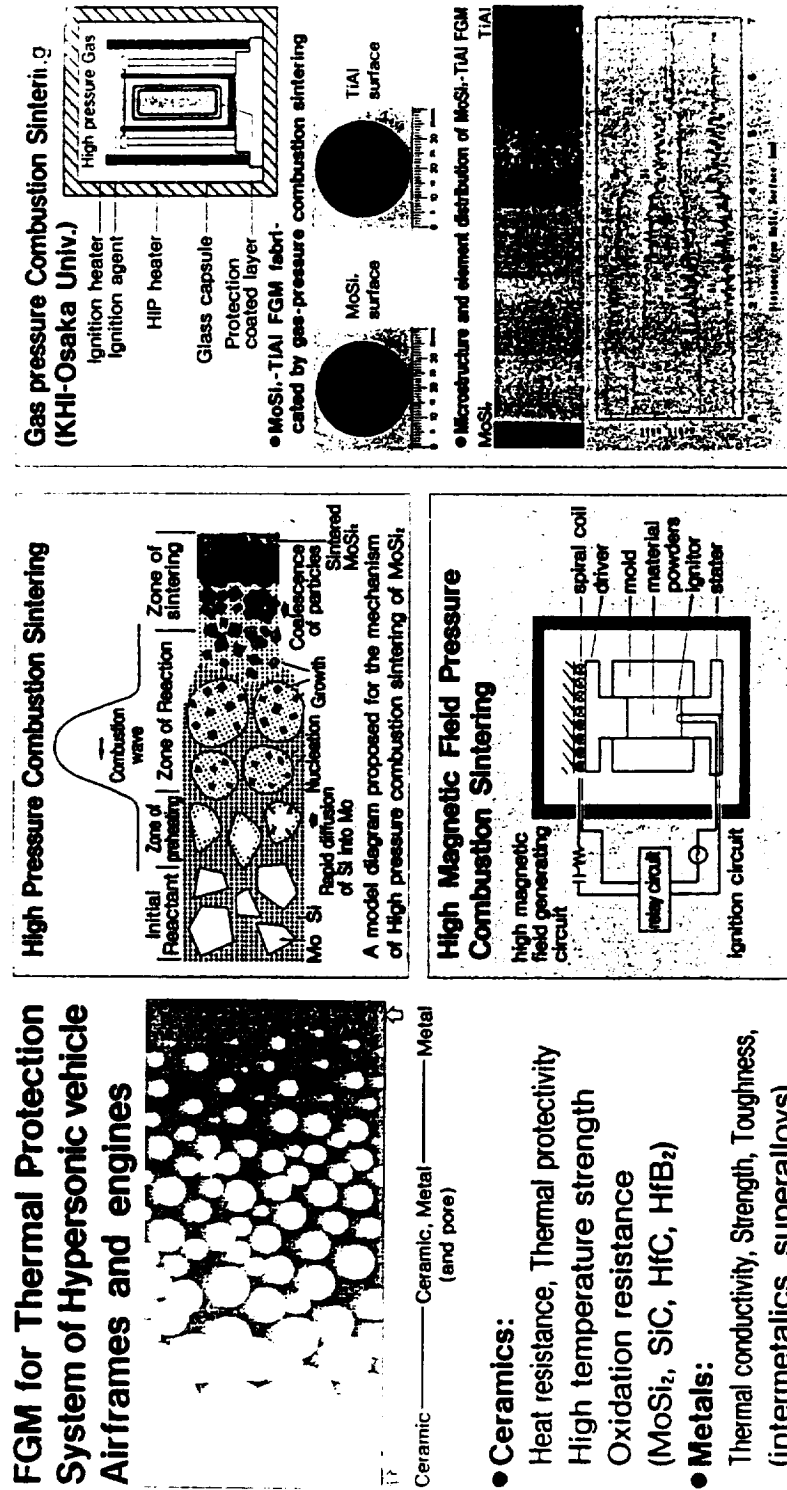
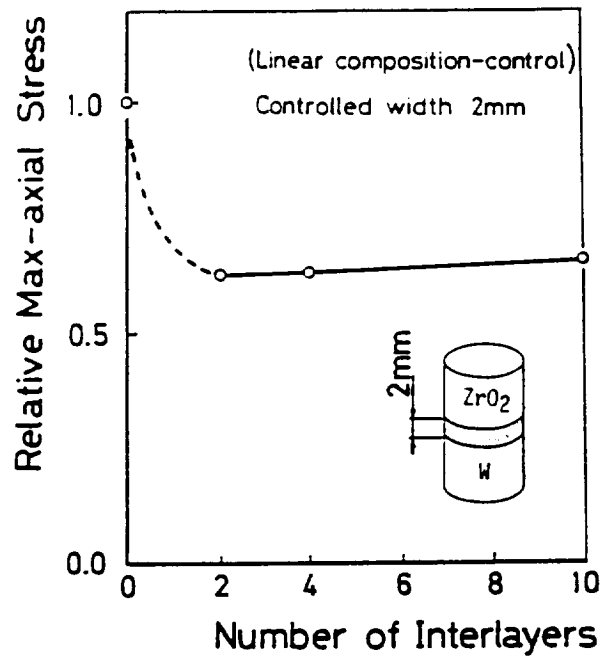
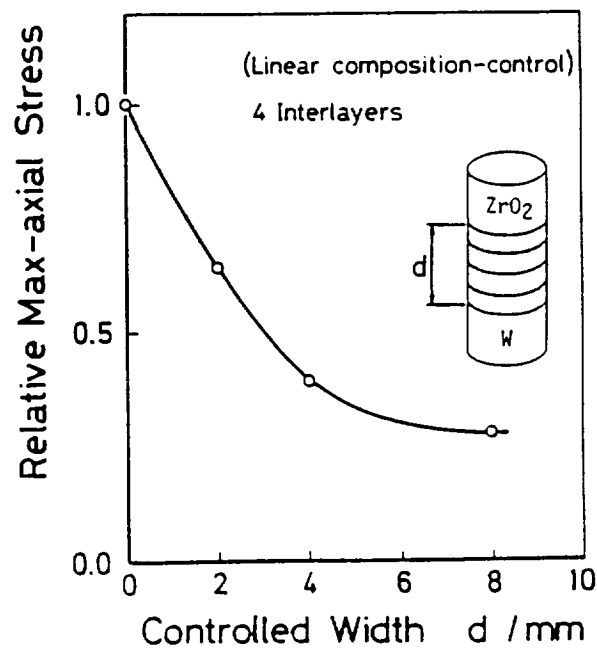


Figure 4.16. Functionally gradient material.



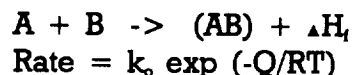
Effect of gradation fineness on relative maximum axial stress.



Effect of interlayer width on relative maximum axial stress.

Figure 4.17.

The always-present Japanese concern with cost-effective production is perhaps one of the reasons that the FGM program has received such a high profile. This attraction may be appreciated by considering the basis of the reactions. For example, consider a reaction of elemental components which can be in the form of powders, plasma spray composites, or gas and powdered metal. The following general reaction can be written:



In this case, the heat of reaction ΔH_r serves to increase the reaction rate, which in turn increases the temperature, which increases the rate of evolution of heat of reaction. This is a fundamental characteristic of autocatalytic reactions which accelerate to a rapid completion. During such reactions there is little time for heat loss to the surroundings, and in the limit of adiabatic conditions the temperature rise is given approximately by $\Delta T = (\Delta H_r L)/C_p$, where L is the latent heat and C_p is the specific heat. For many common reactions involving metal to ceramic transitions, ΔT can easily exceed 1500°C . With these basic kinetic requirements in mind, it is clear that an interlaced network of reactants, called the degree of phase conjugation, is preferred. Furthermore, when the reaction produces a liquid phase, that occurs as a thin layer of the order of 20 microns propagating through the graded material, a high level of densification is possible under an applied external pressure. The reaction is rapid, with propagation velocities in the range from 1-150 mm/s; it can be controlled effectively by using various levels of preheating to increase the rate of reaction or dilution with inert constituents. As a result, the basis behind FGM provides for a rapid production rate of high-temperature materials with relatively little expensive capital equipment.

Conventional approaches to these materials require melting under carefully controlled atmospheres with repeated processing and scrupulous control of metal treatment conditions at each stage. Perhaps the Japanese view this process as a way of circumventing the high cost of many of the U.S. operations.

Currently, one of the main issues remaining in the FGM activity is sample size scale-up. The current program is focused on sample sizes of 30 mm in diameter, and all samples that the JTEC panel saw were of this size. Complex shapes have not been treated as yet but clearly need to be examined. Also, there is at present limited process modeling or control in an analytical sense. Most of the analysis is directed to finite element models of thermal stress (Ref. 4.21, 4.22). Most of the research is done on an empirical basis, using the vast Japanese experience in processing.

GENERAL COMMENTS AND OBSERVATIONS

The Japanese view their commitment in composites as a long-term enterprise without expecting much in terms of short-term payoff. However, basic research in Japan is actually a rather directed, narrowly focused effort almost always driven by product applications. When these applications have not been identified before the initiation of a program, as in the metal matrix composite area, research can move into a holding pattern. Most of the Japanese efforts that the JTEC panel examined have identified processing as a important component in the overall program, but the approach is for the most part empirical. This should not be regarded as a haphazard approach, because the Japanese are quite knowledgeable of the theory, but they do not apply this theory to model processing to the level that is done in the United States or Europe. In fact, there was relatively little use of computers apparent during the JTEC visit.

One self-imposed limitation in the Japanese approach is its overriding reliance on domestic sources for the basic materials. The JTEC panel learned that early in the studies of MMC, the Japanese surpassed their original project goals using AVCO SCS2- and SCS6-produced SiC fibers. They were not able to achieve these goals with the currently available domestic sources of such fibers. As a result, the goals were downgraded to allow for completion of the program objectives using domestically produced fibers.

Often industry uses a parallel approach in MITI projects, where different industrial groups have a common activity basis and share in progress through frequent meetings and interaction. Except for specific cases such as the FGM program, industry has a rather limited interaction with universities. For the most part, industrial laboratories are by far the best equipped in terms of modern state-of-the-art analytical equipment. University laboratories do not always have the advantages of this equipment.

Along with the long-term outlook for major programs in Japan, there is a commitment to a rather large investment in terms of people, money, and facilities. The impact of this investment is often optimized by relatively low mobility in personnel. In fact, a productive research engineer in Japan is encouraged to stay in research rather than to move on to management. Most research engineers in industry have a BS or MS background rather than the PhD that is often found in American industry; however, this should not be regarded as a handicap, because the enthusiasm, hard work, and pride of accomplishment of the personnel in the research institutions visited are most admirable.

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CHAPTER 5

CARBON-CARBON COMPOSITES

James E. Sheehan

INTRODUCTION

It has been known for over twenty years that pyrolysis of the resin in composites composed of carbon fibers in a resin matrix can be used to produce carbon matrix composites with useful properties. These carbon fiber-carbon matrix, or carbon-carbon (C-C), composites are lightweight, high-temperature materials that have found important uses in a variety of rocket propulsion, atmospheric reentry, and high-speed brake applications. Accordingly, the great majority of C-C components that are fabricated throughout the world are used in strategic missiles, space launch vehicles, and aircraft. Because it is apparent that major aerospace and defense activities are developing in Japan, the status and future trends in Japanese C-C science and technology are of significant interest.

The purpose of this chapter is to report on the current state of C-C evolution in Japan and to discuss areas of research and development that could advance the Japanese capability and C-C technology in general. In order to provide a context for the discussion of Japanese C-C activities, the second section of this chapter is a short review of C-C properties, fabrication methods, and applications. Because important future uses for C-C include components for airbreathing engines and parts that experience aerodynamic heating, the subject of oxidation protection is included.

The third section of this chapter describes past and present C-C composite activities in Japan. Here a review is given of available Japanese literature on C-C that has been translated into or at least abstracted in English. After the literature review, separate subsections are devoted to discussions of current government sponsored and privately funded C-C development programs in Japan. Most of this very current information was obtained during the visit of the JTEC panel to Japan

in early February of 1990. Information in these subsections was also obtained from a recently published article on composites activities in Japan.

The final section of this chapter presents an assessment of the Japanese position in C-C technology from the standpoints of both current capabilities and what might be accomplished in the future. Here summaries are given of the present state of the technology and of important materials development trends. Contrasts are drawn between the Japanese position in C-C and that of the United States in terms of past and present influences, manufacturing capabilities and markets, and focal areas in research and development. In total, it is clear that the Japanese know and practice C-C composites fabrication, consider a proficiency with C-C composites as enabling for important commercial and military aerospace activities, and many Japanese also view C-C composites as useful in a variety of commercial nonaerospace applications if processing costs can be reduced.

CARBON-CARBON COMPOSITES

Properties

C-C composites are composed of carbon fibers in a carbon matrix. They are a family of lightweight materials that can perform at very high temperatures and have superior thermal shock, toughness, ablation, and high-speed friction properties. Current defense and aerospace applications are based on these attributes and include rocket nozzle components, atmospheric reentry thermal protection, and aircraft brake discs (Refs. 5.1-5.5).

Although the present applications for C-C composites cannot be considered structural in the sense of sustained primary loading, this is not due to an inherent lack of structural capability. Highly densified C-C composites reinforced in two directions (2-D) with high-performance fibers can have strengths in the principal directions of 250 to 340 MPa and elastic moduli of 90 to 120 GPa. When considering flight-related applications, the most pertinent way of viewing strength is to consider the ratio of strength to density. Figure 5.1 is a plot of this ratio versus temperature for several important aerospace materials and illustrates the unique structural capability of C-C composites. Clearly, C-C composites are unparalleled in terms of strength retention at extremely high temperatures.

Oxidation Protection

The most important uses for C-C composites in future defense and aerospace systems are those in which the materials perform as primary structures. Prominent among these future structural applications are airbreathing engine and hypersonic vehicle components that require extended periods of high-temperature operation

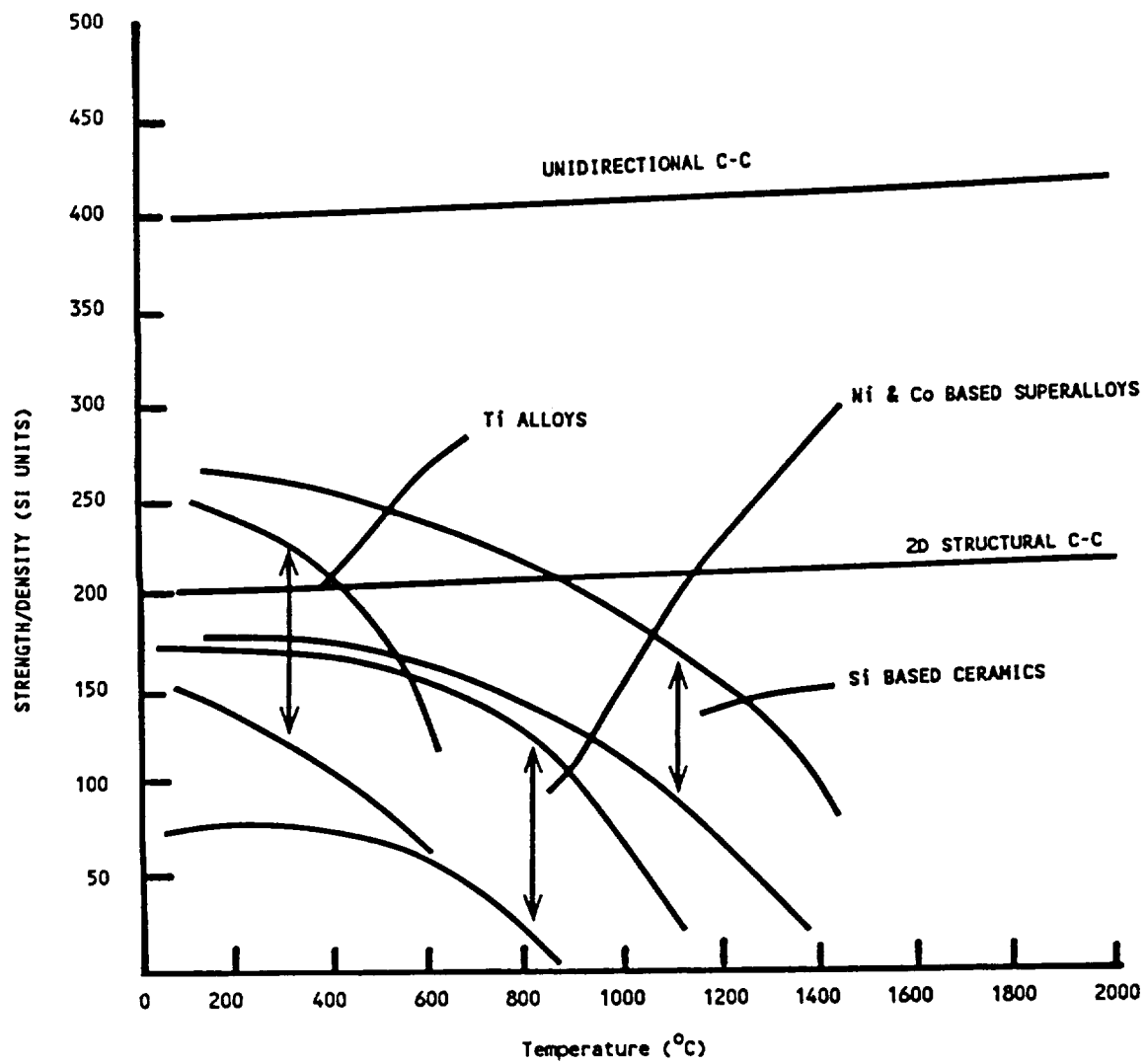


Figure 8.1. Specific strength-versus-temperature comparisons of aerospace materials.

in oxidizing environments. Because the oxides of carbon are volatile and not protective, internal and external coatings are presently being developed for the oxidation protection of structural C-C composites (Refs. 5.6-5.10). It is well known that a coated C-C material is currently used for the nose cap and wing leading edges of the NASA Shuttle Orbiter vehicles. The Shuttle C-C has performed well as a nonstructural thermal protection material with a relatively thick coating system (Ref. 5.9). Providing reliable oxidation protection for structural C-C composites has proven to be a more difficult problem, however. Here the materials have very low thermal expansion coefficients, the components are thin and require thin coatings, very minimal oxidation can be tolerated, and the duty cycles often include substantial time at temperatures where coating defects are most detrimental.

Fabrication

As shown in Figure 5.2, the fabrication of C-C composites initially involves textile processing to produce a carbon fiber preform. The specific technique that is used depends on the required fiber architecture and the component design. Typical processes include fabric weaving, braiding, winding, and the multidirectional weaving of freestanding bodies (Refs. 5.11-5.18). Very often the fabrication includes the use of a resin to rigidize the preform, and includes a procedure in which the fibers are consolidated and the resin is cured to form a carbon fiber-resin matrix composite (Refs. 5.1-5.5). For example, fabric laminates are made by weaving fabric from multifiber carbon yarns, impregnating the fabric with liquid resin, cutting and stacking the impregnated layers, and then compressing the layers while curing the resin. Phenolic resins are frequently used because of their high yield of carbon when decomposed by heating. The use of a rigidizing resin is generally not required for freestanding multidirectional preforms.

Carbon-phenolic preforms are converted to C-C composites by slow heating in an inert gas environment. This initial thermal decomposition or pyrolysis step leaves carbon in place of the resin. At this point the composites are very porous and have poor mechanical properties, so the pores are filled with additional carbon matrix. This is accomplished either by liquid or vapor phase processing (Refs. 5.1, 5.2, 5.18). Liquid processing involves repeated cycles of resin or pitch impregnation, pyrolysis, and heat treatment. Vapor phase densification is conducted in reactors where a flowing hydrocarbon gas infiltrates the part and is thermally decomposed to deposit carbon.

After the C-C parts are processed to achieve the desired bulk density and porosity level, they receive a final machining and nondestructive examination (NDE). Although not shown in Figure 5.2 or mentioned earlier, the densification procedures often include intermittent machining to remove surface deposits, and NDE is very often also conducted after preforming and before the first pyrolysis. Like most synthetic graphite, C-C composites are rather soft but somewhat abrasive, so

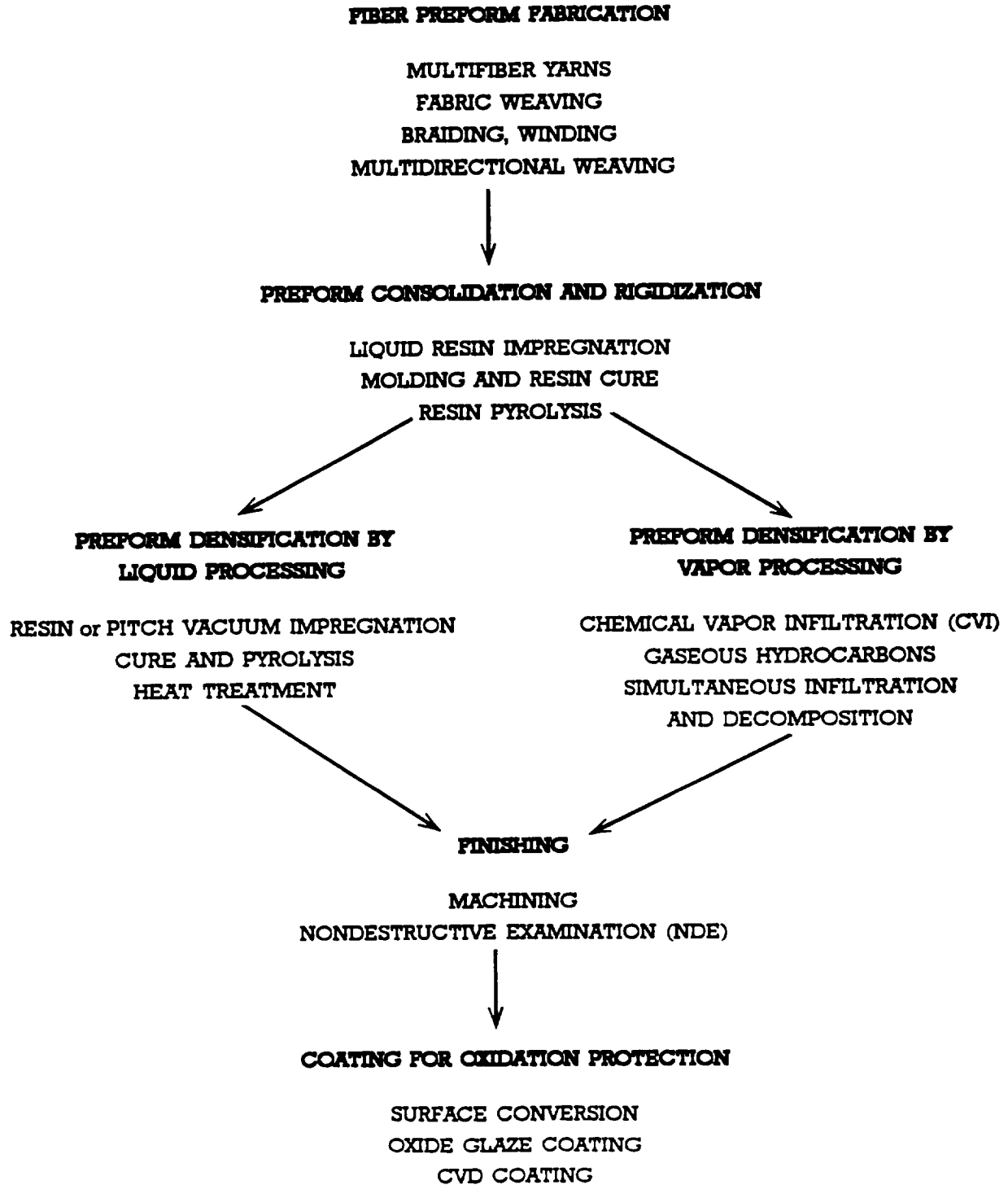


Figure 3.2. Carbon-carbon composites fabrication.

high-speed steel or carbide tools are normally used for machining. In the interest of tool life, diamond tools may be advantageous for some operations. NDE techniques that have been found to be useful include x-ray radiography, ultrasonic inspection, and electrical conductivity measurements.

The application of coatings to parts that require oxidation protection is the final phase of C-C processing. This often involves an initial chemical surface treatment to improve coating adherence. For example, the surface may be converted to a carbide by exposure to appropriate reactants at high temperatures (Refs. 5.7, 5.9). A number of different coatings and coating methods have been developed to provide oxidation protection. Prominent among these are the application of dense carbide coatings by chemical vapor deposition (CVD) and the use of various approaches to form oxide glasses and glazes (Refs. 5.7-5.10).

Applications

The majority of the C-C material currently being produced is in the form of high-temperature components for missiles and military aircraft. The most important applications include reentry bodies, rocket nozzles, and exit cones for strategic missiles, and brake discs for military aircraft (Refs. 5.1-5.5). In recent years two commercial aerospace applications--brake discs for transport planes and rocket propulsion components for satellite launch vehicles--have also become prominent. Also notable is the coated C-C used for the nose cap and wing leading edges on the Shuttle Orbiter vehicles (Refs. 5.5-5.9). The present commercial industrial applications for C-C composites, such as hot glass handling tools and hot press dies and pistons, are very minor compared to the uses in defense and aerospace.

A 1985 world market study for C-C composites conducted by C. H. Kline & Company estimated growth in the industry at about 15 percent per year (Ref. 5.19). This would put 1989 sales at about \$200 million with the manufacture of about 2.3×10^6 kg of material. In terms of dollars, the Kline study showed sales to be about equally divided between reentry bodies (37 percent), nozzles and exit cones (31 percent), and brakes (31 percent). In terms of weight, almost two-thirds of the C-C is in the form of brake discs (63 percent), while nozzles and exit cones (14 percent) and reentry bodies (11 percent) are limited-production, more costly items. Miscellaneous items such as the C-C used in commercial nonaerospace applications constituted only about 1 percent of sales and about 12 percent of weight. It is estimated that 75 to 80 percent of the world production of C-C is carried out in the United States, with most of the remainder in Europe and the USSR. The manufacture of C-C composites in Japan is thought to be 1 percent or less of the world total.

It is likely that the most important future applications for C-C composites will be in the aerospace and defense industries. The use of C-C brake discs on

commercial transport aircraft has become a significant business in the past several years and is expected to grow in the future. It is clearly more difficult to predict the future for C-C composites in advanced military and aerospace applications because the materials are developmental and the projected systems will require continued government support. Specific examples in this area include hot section components for limited-life missile engines, exhaust parts for advanced fighter aircraft, hypersonic vehicle fuselage and wing components, and structures for space defense satellites.

Commercial nonaerospace applications for C-C composites are minor at this time because of the relatively high cost of the material. Expanded use of C-C in industries other than defense and aerospace will most likely require the development of methods that reduce cost and yet maintain the properties that provide performance advantages. Near-term uses that are often cited are high-speed train and special automobile brakes, clutch pads, furnace heating elements, forging dies and melting crucibles, corrosive chemical reactors and heat exchangers, prosthetic devices, and components for internal combustion engines (Refs. 5.1, 5.2). Potential further term uses include plasma limiters for nuclear fusion devices and inert gas ducting and heat exchangers for high-temperature, gas-cooled fission reactors.

CARBON-CARBON COMPOSITES IN JAPAN

Literature Survey

Published Japanese studies of C-C composites span almost twenty years and roughly coincide with similar work conducted in the United States and Europe. Japanese papers that have been published in English appear rather infrequently and tend to be brief and lacking in detail. Nevertheless, the work has been pertinent, timely, and apparently well executed. Most of the Japanese literature that has appeared in English is of a basic nature and addresses the relationships between processing, microstructure, and properties.

Beginning in the early 1970s and extending to the present, several Japanese investigators have been concerned with how process parameters and choice of materials affect matrix microstructure, bonding between the matrix and fibers, and the resulting composite properties. Studies conducted at the Tokyo Institute of Technology are particularly prominent in the literature. The interaction between carbon fibers and carbon matrix materials that are derived from resins has received a good deal of attention (Refs. 5.20, 5.21, 5.23, 5.25, 5.26). It has been shown that stress-induced graphitization occurs in the matrix and that heat treatment temperature has a strong influence on composite properties.

Matrix materials in C-C composites that were produced by pitch pyrolysis and chemical vapor infiltration (CVI) have also been studied in Japan (Refs. 5.22, 5.24, 5.28). Here it was determined that matrix microstructure and the degree of bonding between the fibers and matrix are strong functions of the processing parameters and that these factors are crucial to developing the desired composite properties. This work parallels similar investigations carried out in the United States, where the results are in general agreement with those obtained in Japan (Refs. 5.29-5.31).

The oxidation of C-C composites has also been studied in Japan. For example, microstructure investigations and oxidation rate measurements have shown that initial oxidation occurs preferentially at the interface between the fibers and the matrix, and that the activation energy for oxidation suggests that induced stress at the interface influences the oxidation process (Ref. 5.32). The subject of oxidation in relation to C-C friction and wear for brake applications has also been addressed in the Japanese literature (Ref. 5.33). On the other hand, no papers were found on work pertaining to coatings or additives for oxidation protection of C-C composites. It should be mentioned, however, that U.S. patents have been granted to Japanese inventors for methods of protecting carbon fibers and porous carbon bodies from oxidation (Refs. 5.34-5.36). The approaches involve borate and phosphate glasses and are similar to techniques currently being used in the United States for C-C oxidation protection (Refs. 5.6, 5.7).

The technical papers cited in this section usually contain only a brief description of the procedures used to fabricate the C-C composites. Very often the studies were conducted on strands of carbon fiber that contained a matrix but had not been consolidated into what could be considered a composite article. Little is apparently available in the Japanese literature on the important C-C fabrication procedures of fiber preforming to establish shape and fiber architecture or on the liquid or vapor phase densification methods that are normally required to produce bodies of high integrity. However, it is known from the visit of the JTEC panel to Japan and a recent description of Japanese C-C activities that the Japanese are currently fabricating C-C components in much the same manner as is practiced in the United States and Europe (Ref. 5.37). As examples, rocket motor exit cones are produced at Nissan Motors using U.S. C-C technology, and Nippon carbon produces a variety of C-C shapes by what can be considered conventional C-C processing.

As will be discussed in later sections, it is clear that efforts are being made in Japan to abbreviate the costly and time-consuming processing that is normally used for producing C-C parts (Ref. 5.38). Of particular interest is a recent U.S. patent granted to Japanese inventors that describes a process for impregnating continuous multifiber carbon yarns with a mixture of pitch and coke particles (Ref. 5.39). The impregnated yarns are coated with a thermoplastic resin that

prevents the matrix precursor powders from being lost during handling and subsequent processing. Textile methods can then be used to make preformed parts containing the matrix precursor powders. It has been demonstrated that 2-D fabric laminate C-C composites made from impregnated yarns of high-performance carbon fibers by a one-step process of simultaneous pressing and pyrolysis have bend strengths of about 96 MPa. A recent paper describing the process and the properties of C-C made from several different preformed yarns reports strengths between 414 and 670 MPa for unidirectionally reinforced material (Ref. 5.40).

Current Activities for Government Projects

The Japanese government has identified the aerospace industry as vital to continued economic growth. A long-term commitment has been made for combined government and private support of projects that are considered essential to establishing a competitive position in aerospace. Present generation satellite launch activities involve the use of C-C composite rocket nozzles and exit cones, and it is known that the capability to fabricate these components exists in Japan. Furthermore, current Japanese projects to develop advanced aerospace vehicles emphasize C-C technology, and these projects are providing the impetus for the evolution of new and improved C-C composites.

The specific Japanese government programs that provide for the development of advanced C-C composites are the High-Performance Materials for Severe Environments Project (Project 5) and the project to develop a Japanese space shuttle vehicle (HOPE). Project 5 was started in 1989 and will run in its present form until 1996. The purpose of Project 5 is to develop new high-temperature structural materials that will aid the development of advanced aircraft and spaceplanes. Project 5 is supported by the Agency of Industrial Science and Technology (AIST) which operates under the Ministry of International Trade and Industry (MITI). A total of twelve organizations are participating in Project 5, of which five are using PAN-based fibers and coal-based fibers and eight are working on petroleum pitch-based carbon/carbon. The HOPE project encompasses the development of a single vehicle and includes the fabrication of oxidation-protected C-C test specimens and prototype components. HOPE is supported by the National Space Development Agency (NASDA). Table 5.1 lists some of the participants and gives a brief description of C-C activities being conducted for Project 5 and HOPE.

Interesting fabrication work is being conducted at the Government Industrial Research Institute (GIRI) in Kyushu. The Kyushu GIRI program includes the investigation of three novel methods for abbreviating the fabrication of carbon fiber composites. One method is based on the use of mesophase pitch to form the carbon matrix. It involves oxidative cross-linking of the pitch and heat

Table 8.1
Some Participants and C-C Activities in Project 5 and HOPE

Participants	Activities
<u>Project 5</u>	
* Kyushu GIRI	Novel Fabrication Methods Oxidation Protection
* Kobe Steel	Fabrication and Properties Studies
Nippon Steel	Specifics Not Identified
Fuji Heavy Industries	Specifics Not Identified
<u>HOPE</u>	
* Kawasaki Heavy Industries	Prototype Components Fabrication Oxidation Protection Development
Mitsubishi Heavy Industries	Prototype Components Fabrication

* Visited by the JTEC panel

treatment at temperatures up to 2600°C. Unidirectional composites are being made without densification after heat treatment that have densities of about 1.6 g·cc⁻¹ and bending strengths of 970 MPa. In a second method, oxidized pitch fibers are being molded directly into test pieces, and then the pieces are carbonized and heat treated. Bending strengths between 200 and 400 MPa have been achieved by this technique. In a third approach, fibers carbonized at low temperatures are immersed in anthracene oil and then pressed, carbonized, and heat treated. Heat treatment at 2600°C has produced test specimens with densities of about 1.6 g·cc⁻¹ and bend strengths as high as 540 MPa.

Efforts are also underway at the Kyushu GIRI to investigate various approaches to C-C oxidation protection. This work has only started recently and the activities include the evaluation of fiber coatings, matrix additives, and external coatings.

The work at Kobe Steel for Project 5 appears to be focused on the fabrication and testing of 2-D C-C fabric laminates. Composites containing high-performance fibers derived from both pitch and polyacrylonitrile (PAN) are being made.

Composite densification involves pitch impregnation, pressure pyrolysis, and heat treatment. Current C-C materials with densities in the 1.65 to 1.75 g·cc⁻¹ range have shown strengths between 300 and 400 MPa.

Kawasaki Heavy Industries and Mitsubishi Heavy Industries are industrial giants that are involved in developing hardware for the Japanese space effort. Both are fabricating C-C prototype nose cap and wing leading edge components for the HOPE vehicle. The work at Kawasaki on external coatings for oxidation protection is apparently based on a two-layer SiC concept where the SiC coatings are made by chemical vapor deposition. The inner coating has a low density for compliance, while the other layer is dense and acts as the primary oxidation barrier.

Current Private Activities

During the visit of the JTEC panel to Japan, meetings were held with five companies that are active in C-C development but were not at the time participants in Project 5 or the HOPE project. The first of these meetings was at the NKK Research Center. NKK is a large steel-making, ship-building, and construction company that is diversifying into electronics, biotechnology, and advanced materials. Efforts at NKK are currently focused on the cost-effective fabrication of C-C friction materials for the automotive industry, although NKK is also interested in electrical and biomedical applications. In order to reduce C-C cost and processing time, NKK is developing a process of pitch injection molding and rapid pyrolysis to densify carbon fiber preforms.

Across Company is a small company that is in the business of developing and manufacturing C-C parts for commercial industrial applications. Across is fabricating C-C shapes by hot pressing carbon fiber preforms in which the yarns have been impregnated with a mixture of pitch and coke particles (Refs. 5.39, 5.40). This unique fabrication method was developed in collaboration with the Institute of Industrial Science at the University of Tokyo and is designed to produce material with attractive properties at low cost. Across has targeted furnace heating elements, friction materials, and fuel cell components as near-term applications.

Nippon Carbon Company is a medium-sized company whose principal product is synthetic graphite electrodes for electric arc steel-making furnaces. Nippon Carbon also manufactures material for graphite heat exchangers, activated carbon products, specialty graphites, carbon and SiC fibers, and C-C composites. The development of C-C composites has been an activity for over 10 years, and current processing is the same as used in the United States and Europe. Most of the materials are fabric laminates or wound structures that are preformed and densified with a resin-pitch mixture. Composites containing high-performance PAN precursor

fibers exhibit strengths in the 250 to 300 MPa range. Current applications include industrial furnace parts, hot press dies and pistons, and glass-handling tools. Important future applications of interest are friction materials, metal processing components, and biomaterials. A wide variety of impressive C-C components of different shapes and some of large size were displayed at the Nippon Carbon plant.

Visits were also made to Tonen and Nippon Oil Company. Both companies manufacture high-performance carbon fibers and fabricate C-C composite materials by conventional processing methods using pitch and pitch-resin mixtures. Nippon Oil is using high-modulus and high-strength pitch-based fibers. Carbon fiber oxidation is being studied at Tonen, and CVD SiC and Si₃N₄ fiber coatings are being developed for oxidation protection. Fiber coatings of CVD SiC are also being investigated at Nippon Oil, along with external coatings for C-C composites. In parallel with work being conducted in the United States, the external coating systems are composed of a glass sealant and CVD SiC.

STATUS OF C-C TECHNOLOGY IN JAPAN

Present Capabilities and Important Trends

It must be pointed out that in addition to the companies discussed earlier, it is known that at least seven other Japanese companies are involved in the fabrication and development of C-C composites. These companies are Hitachi Chemical, Kawasaki Steel, Mitsubishi Rayon, Ohwada Carbon, Toho Rayon, Toray Industries, and TYK Corporation. Clearly there has been significant interest in C-C composites by Japanese industry for some time, and yet per annum production of C-C components in Japan is probably less than 1 percent of the world total. As pointed out earlier, the principal current markets for C-C are in defense and recently in commercial aerospace. These are fledgling industries in Japan and they represent markets in the United States and Europe that are not easily penetrated by foreign sources.*

The fabrication, characterization, and testing of C-C composites have been activities in Japan for over fifteen years. Japan has a strong carbon fiber industry and has established the weaving, preforming, and consolidation technology needed for a very competitive position in resin matrix composites. Because this is the same technology used in C-C fabrication, and a mature Japanese synthetic graphite industry possesses the equipment and know-how for the carbonization, heat treatment, and densification steps, a lack of markets is the only significant reason that C-C composites are not produced in Japan in much larger quantities.

* MITI states that Japanese companies are working to apply their new materials to consumer products.

It is interesting that, like the rest of the world, the Japanese have not found major commercial nonaerospace markets for C-C composites. The general feeling is that the high cost of C-C is the major barrier here, and that methods must be found to replace the lengthy and expensive densification cycles currently needed to produce materials with attractive properties. As discussed above, the development of new cost-effective processing techniques that abbreviate the fabrication of C-C composites is a topic receiving considerable attention in Japan.

Oxidation protection for C-C composites is a second important development area because a wide range of potential applications require the materials to perform at high temperatures in oxidizing environments. It is clear that effective and reliable oxidation protection would make C-C composites extremely important high-temperature materials. Programs to develop external coatings and methods of internal protection for structural C-C composites have received significant government funding in the United States for over a decade. In contrast, C-C oxidation protection is a new area of investigation in Japan. Although the methods that have been found to be fruitful are known by the Japanese, the fabrication and test experience needed for proficiency in the technology will only be achieved by several years of rather intense effort.

Contrasts Between Japan and the United States

Table 5.2 lists capsule assessments of key areas that contrast the evolution, status, and expectations for C-C composites in Japan and the United States. In terms of basic research, both countries have had a parallel low level of sustained activity for almost two decades, and it is unlikely that this will change in the near future. Most of the Japanese work has been conducted at universities. The bulk of the basic work on C-C in the United States has been carried out at government laboratories and at private companies using government funds; however, greater participation by universities seems to be a recent trend in the United States.

Applied research for C-C composites has received significant attention in the United States for the past ten years because of important new applications in aircraft, missiles, and defense satellites. The recent Japanese pursuit of a competitive position in aerospace and defense has provided an impetus for C-C applied research efforts similar to those being conducted in the United States. The same is true of C-C component development. This has been a major government funded activity in the United States since C-C composites were found to have attractive ablation and thermal shock properties. Rocket propulsion components for satellite launch applications have been fabricated in Japan for a number of years, and now that a broad emphasis is being placed on aerospace applications, greater attention will be given to the design analysis and preforming methods needed for the fabrication and integration of C-C parts with optimum properties.

Table 8.2
Comparative Assessments of C-C Composites Work
In Japan and the United States

Area	Japan	U.S.
Basic Research	Low level of effort for almost 20 years	Comparable to Japanese effort
Applied Research	Increased activity in past several years	Significant emphasis in past 10 years
Component Development	Lack of applications has been a hindrance but current aerospace projects will advance the technology	Major government funded activity for almost 20 years
Manufacturing	Several companies have the facilities and basic know-how but lack broad experience	Mature industry capable of producing large complex shapes
Markets	Currently minimal for both government and private sector	Significant for government and commercial aircraft brake applications
Current Applied R&D Emphasis	Prototype components, oxidation protection cost-effective fabrication	Structural properties, oxidation protection, manufacturing science, prototype components
Expected Future Applications	Space vehicles, advanced transport aircraft, commercial friction materials, industrial heating and materials processing hardware	Missile propulsion, fighter aircraft exhaust components, hypersonic transport, space structures

The manufacture of large and complex C-C components is well established in the United States. A mature domestic industry has demonstrated the fabrication methods, process control, and verification techniques necessary to manufacture reproducible and reliable finished components. In contrast, although several Japanese companies certainly possess the facilities and basic understanding of conventional C-C fabrication to produce parts on a reasonable scale, a lack of applications and lack of opportunity to develop broad manufacturing and design experience must be recognized as a current limitation. The United States manufacturing capability was established in response to a large sustained demand for C-C components that are used in strategic missiles and military aircraft. Japan has not benefitted from a comparable demand.

Recent applied research and development activities in Japan in support of government projects include the fabrication of prototype components for the HOPE spaceplane and oxidation protection for HOPE and supersonic/hypersonic transport applications. In these areas, it is clear that the component development and oxidation protection experience gained in a number of long-term programs for current and advanced applications has given the United States a considerable technological lead. This is also true for aircraft brakes and friction materials in general. In contrast, the Japanese are very concerned with the cost of C-C composites and with identifying nonaerospace applications for the materials. Their efforts to develop new cost-effective fabrication methods and in turn open the door to broad uses as friction materials, heating elements, and materials processing hardware in commercial industries mark a trend that appears to be absent in the United States.

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APPENDICES

A. PROFESSIONAL EXPERIENCE OF PANEL MEMBERS

R. Judd Diefendorf (Chairman)

R. Judd Diefendorf holds the McAlister Trustees Chair in Advanced Engineering Materials and is a Professor of Ceramic Engineering at Clemson University. Prior to his current appointment, he served as Director of the ONR/DARPA High Temperature Advanced Structural Composites (HiTASC) Program and Professor of Materials Engineering at Rensselaer Polytechnic Institute (RPI). His current areas of interest include asymmetric coupling in composites, shape stable composites, manufacturing of low-cost composites, ceramic matrix composites, and high-strength fibers. Professor Diefendorf received his B.S. degree in Chemistry from the University of Rochester in 1953 and his Ph.D. degree in Physical Chemistry from the University of Toronto in 1958. He was a Scientist at the Missile and Ordnance Systems Department, General Electric Company (1958-59) and at the General Electric Research Laboratory (1960-65), where he pioneered research on fabricability and properties of pyrolytic graphite as a reentry and rocket nozzle material, and on boron filament deposition. He has lectured on composites for NATO AGARD; received the Cordiner Award at GE; the best paper award with G. Maher from IEEE; the Humboldt-Stiftung Award for Research and Teaching; and most recently was elected a Fellow of ASM. Professor Diefendorf has received 23 U.S. patents and has published over 100 technical papers. He has served on numerous National Materials Advisory Board committees, the Scientific Advisory Board, and Division Advisory Group of the Aeronautical Systems Division of the Air Force, and the Board of Governors of the Gordon Conferences.

Salvatore J. Grisaffe

Salvatore J. Grisaffe was appointed as Chief of the Materials Division at the National Aeronautics and Space Administration's Lewis Research Center in 1983. A member of the Senior Executive Service, his career at Lewis spans 32 years. Prior to that promotion, he served as Chief, Materials Applications and Technology Branch; Chief, Surface Protection Branch, and Head, Coatings Section. Grisaffe

earned his bachelor of science degree in metallurgical engineering from the University of Illinois and a master of science degree from Case Institute of Technology (now Case Western Reserve University). He also completed the Harvard Graduate School of Business Administration's Program for Management Development under a NASA fellowship. Grisaffe is responsible for leading his division in the search for new materials and processes, as well as in developing an understanding of key material-related phenomena. These new materials, processes and understanding are then applied to advanced NASA systems in the areas of aeropropulsion, space propulsion, space power, and space applications. When Grisaffe was personally conducting research, he specialized in high temperature coatings, ceramics and power system/aerospace propulsion system materials. Grisaffe has authored 60 technical papers and book chapters and has been awarded six U.S. patents. He has served on several National Materials Advisory Board committees. In addition, he is a Fellow of the American Society for Metals, and has been active in many other professional societies. He has received numerous NASA achievement awards as well as the the Presidential Meritorious Executive Rank Award.

William B. Hillig

Dr. William B. Hillig is currently a Visiting Professor in Materials Engineering at the Rensselaer Polytechnic Institute in Troy, NY, following his 35-year career at the GE Corporate Research and Development Laboratory. He received a Ph.D. in physical chemistry from the University of Michigan in 1953, whereupon he joined GE. His positions there included Research Scientist, Liaison Scientist, and Manager. His research includes fundamental studies of nucleation and growth kinetics of crystalline solids from liquids and glasses, basic studies regarding intrinsic strength and strength-controlling mechanisms in brittle materials. More recently his work has focused on composites: the processing of ceramic matrix composites, micromechanical modeling of failure mechanisms in ceramic and other matrix composites, and predictions of ultimate capabilities. He is a Fellow of the American Ceramic Society and of the American Academy for the Advancement of Science, and is a member of the American Chemical Society and the New York Academy of Science. He has written many widely-cited papers, reviews, and book contributions in the above fields, and is the author of more than 15 patents. He has served on various governmental advisory committees, including an evaluation panel of the National Bureau of Standards (now the National Institute of Standards and Technology).

John H. Perepezko

John Perepezko has been a Professor of Materials Science and Engineering at the University of Wisconsin-Madison since 1975. His current research interests focus on materials synthesis and processing and include the solidification processing of

high-temperature intermetallic matrix composites, interfacial reactions, interdiffusion and high-temperature phase stability of composites and coatings, rapid solidification of powders, containerless materials processing and nucleation phenomena. He is a Fellow of the American Society for Metals, Chairman of the NASA Metals and Alloys Discipline Working Group and a member of the Solid State Sciences Committee of the National Research Council. Dr. Perepezko received his B.S. and M.S. from the Polytechnic Institute of New York and his Ph.D. from Carnegie Mellon University

R. Byron Pipes

R. Byron Pipes has served as the Dean of the College of Engineering and Robert L. Spencer Professor of Engineering at the University of Delaware since 1985. Previously, he served as Director of the Delaware Center for Composite Materials from 1977 to 1985. Professor Pipes was elected to the National Academy of Engineering in 1987, and has served on the National Materials Advisory Board and the Aeronautics and Space Engineering Board. His current research interests include manufacturing science for high performance composite materials.

James E. Sheehan

Dr. Sheehan has 18 years of experience in high-temperature materials research and development. For the past 10 years he has specialized in carbon and ceramic composites and has been particularly interested in oxidation protection for carbon-carbon composites. Dr. Sheehan has been the program manager or principal investigator for a number of Air Force, Navy, and DARPA funded programs to develop external coatings and internal oxidation inhibitors for carbon-carbon composites and is currently the manager of a major Air Force program to develop oxidation resistant coatings for carbon fibers. In addition to conducting specific experimental investigations, Dr. Sheehan has presented and published reviews and assessments of carbon-carbon oxidation protection technology for NASA, the National Materials Advisory Board, the Institute for Defence Analysis, the American Carbon Society, and the American Ceramic Society. His most recent contributions include the monograph "Ceramic Coatings for Carbon Materials" and a chapter entitled "Coatings on Carbon Fibers and Carbon-Carbon Composites," for the book *Carbon-Carbon Materials and Composites* edited by John D. Buckley of NASA Langley Research Center.

B. JAPANESE ORGANIZATIONS AND FACILITIES VISITED

Tokyo	MITI/Agency of Industrial Science & Technology (AIST) National Research Institute for Metals National Aerospace Laboratory Ube Industries, Ltd. Tonen Corporation (Corporate R&D Laboratory) Nippon Carbon Co., Ltd. Kobe Steel, Ltd. Across, Ltd.
Sendai	Tohoku University Tohoku Government Industrial Research Institute
Tsukuba	Sumitomo Chemical Co. (Tsukuba Research Laboratory)
Gifu	AIST/ Mechanical Engineering Laboratory
Kawasaki	NKK Corporation (Central Laboratory) Kawasaki Heavy Industries, Ltd. Nippon Steel Corp. (Materials Research Center)
Hitachi City	Hitachi, Ltd. (Hitachi Research Laboratory)
Nagoya	Nagoya Government Industrial Research Institute
Osaka	Osaka Government Industrial Research Institute Osaka University Kobe Steel ,
Yokohama	Nippon Oil Central Research Laboratories
Tosu	Kyushu Government Industrial Research Institute
Ube City	Ube Laboratory, Ube Industries

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